Supporting Information

Metal- and solvent-free direct C-H thiolation of aromatics with sulfonyl chlorides

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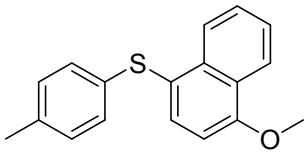
1. General information:

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using $CDCl_3$ as solvent and TMS as an internal standard. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (EI) were obtained with the Agilent Technologies 7250 GCQTOF. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. Column chromatography was performed using silica gel (200-300 mesh). Reagents were used as received from commercial suppliers without further purification.

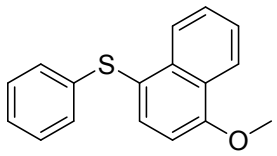
2. General procedure for reaction:

p-Tolsulfonyl chloride (0.4 mmol, *if solid*), TMAI (0.1 mmol) were added to an oven-dried reaction vessel equipped with a magnetic stirring bar, then the vessel was purged with oxygen for three times and *p*-tolsulfonyl chloride (0.4 mmol, *if liquid*), 1-methoxynaphthalene (0.2 mmol), $(EtO)_2P(O)H$ (0.4 mmol) were added by syringe. The vessel was sealed and stirred at 100 ^{o}C for 18 hours. After the reaction completed, the reaction mixture was diluted with ethyl acetate and washed with saturated sodium thiosulfate solution. The organic layer was concentrated under reduced pressure to yield the crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 50:1) to give the desired product **3aa** in 90% yield as a pale-yellow oil.

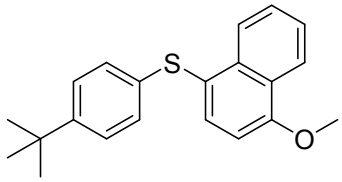
3. Characterization data of products



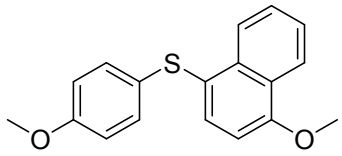
(4-Methoxynaphthalen-1-yl)(*p*-tolyl)sulfane (3aa):[1] Yellow oil, yield: 50.4 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.34-8.29 (m, 2H), 7.74 (d, J = 8.0 Hz, 1H), 7.53-7.47 (m, 2H), 6.97 (s, 4H), 6.80 (d, J = 8.0 Hz, 1H), 4.02 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.8, 135.1, 135.0(5), 134.9(9), 129.6, 127.5, 127.2, 126.5, 125.9, 125.6, 122.5, 120.9, 104.0, 55.6, 20.9.



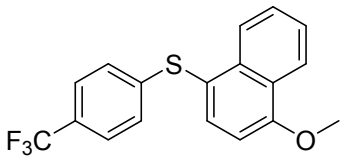
(4-Methoxynaphthalen-1-yl)(phenyl)sulfane (3ab):[1] White solid, yield: 43.7 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.30 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.52-7.48 (m, 2H), 7.15-7.11 (m, 2H), 7.05-7.01 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 139.0, 135.8, 135.2, 128.8, 127.6, 126.6, 125.9, 125.7, 125.0, 122.5, 120.0, 104.0, 55.6.



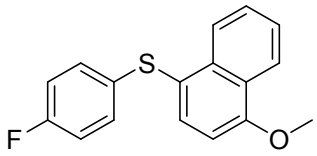
(4-(*tert*-Butyl)phenyl)(4-methoxynaphthalen-1-yl)sulfane (3ac): Yellow solid, yield: 52.2 mg, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.35 (m, 1H), 8.32-8.30 (m, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.53-7.47 (m, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 3.99 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 148.2, 135.4, 135.3, 135.2, 127.5, 126.7, 126.5, 126.0, 125.9, 125.6, 122.5, 120.6, 104.0, 55.6, 34.3, 31.2. HRMS (EI) m/z calcd. for $C_{21}H_{22}OS$: 322.1387, found: 252.1185.



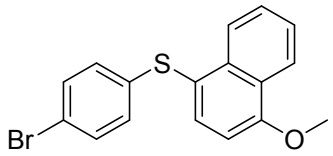
(4-Methoxynaphthalen-1-yl)(4-methoxyphenyl)sulfane (3ad):[2] Yellow oil, yield: 54.0 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.9 Hz, 1H), 8.29 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.53-7.45 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.75-6.72 (m, 3H), 3.96 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 156.3, 134.5, 133.7, 130.1, 128.5, 127.3, 126.4, 125.7, 125.6, 122.4, 114.6, 103.9, 55.5, 55.2.



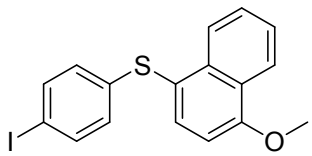
(4-Methoxynaphthalen-1-yl)(4-(trifluoromethyl)phenyl)sulfane (3ae): White solid, yield: 48.1 mg, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36-8.33 (m, 1H), 8.25-8.21 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.54-7.50 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 144.7, 136.6, 135.2, 128.0, 126.8 (q, *J* = 32.4 Hz), 126.7, 125.9, 125.6(4), 125.5(7), 125.5(3), 125.4(9), 122.8, 118.1, 104.1, 55.7. HRMS (EI) m/z calcd. for $C_{18}H_{13}F_3OS$: 334.0636, found: 334.0634.



(4-Fluorophenyl)(4-methoxynaphthalen-1-yl)sulfane (3af):[1] Yellow oil, yield: 47.7 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32-8.28 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.51-7.48 (m, 2H), 7.04-7.01 (m, 2H), 6.86-6.82 (m, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (d, *J* = 243.2 Hz), 157.0, 135.3, 134.8, 133.7 (d, *J* = 3.1 Hz), 128.8 (d, *J* = 7.8 Hz), 127.6, 126.5, 125.7 (d, *J* = 2.3 Hz), 122.6, 120.6, 116.0, 115.8, 103.9, 55.6.

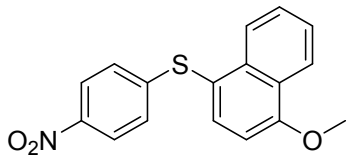


(4-Bromophenyl)(4-methoxynaphthalen-1-yl)sulfane (3ag):[1] Yellow solid, yield: 50.4 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.31 (m, 1H), 8.26-8.23 (m, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.53-7.48 (m, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 138.4, 136.1, 135.0, 131.7, 127.9, 127.8, 126.6, 125.8, 125.7, 122.6, 119.2, 118.5, 104.0, 55.6.

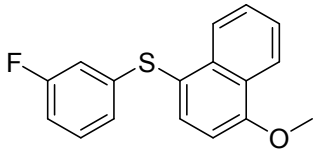


(4-Iodophenyl)(4-methoxynaphthalen-1-yl)sulfane (3ah): Yellow solid, yield: 55.0 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.30 (m, 1H), 8.25-8.22 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.52-7.48 (m, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 2H),

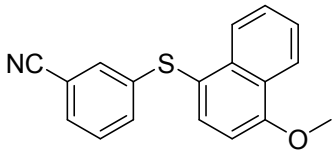
4.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 139.4, 137.6, 136.1, 135.0, 128.2, 127.8, 126.6, 125.8, 125.7, 122.6, 119.0, 104.0, 89.3, 55.6. HRMS (EI) m/z calcd. for $C_{17}H_{13}IOS$: 391.9726, found: 391.9723.



(4-Methoxynaphthalen-1-yl)(4-nitrophenyl)sulfane (3ai):[1] Orange solid, yield: 30.0 mg, 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.35 (m, 1H), 8.17-8.14 (m, 1H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.55-7.52 (m, 2H), 7.00-6.98 (m, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 149.6, 144.9, 136.9, 134.9, 128.2, 126.7, 126.1, 125.3, 124.0, 123.9 122.9, 116.8, 104.1, 55.8.

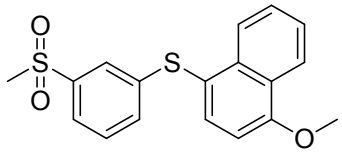


(3-Fluorophenyl)(4-methoxynaphthalen-1-yl)sulfane (3aj): Yellow oil, yield: 38.1 mg, 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.26 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.52-7.50 (m, 2H), 7.10-7.06 (m, 1H), 6.84-6.79 (m, 2H), 6.74-6.69 (m, 1H), 6.64-6.62 (m, 1H), 4.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 246.0 Hz), 157.5, 141.9 (d, *J* = 8.2 Hz), 136.4, 135.2, 129.9 (d, *J* = 8.6 Hz), 127.8, 126.7, 125.8 (d, *J* = 7.8 Hz), 125.1, 122.7, 121.8, 118.8, 113.0 (d, *J* = 23.7 Hz), 111.8 (d, *J* = 21.4 Hz), 104.0, 55.7. HRMS (EI) m/z calcd. for $C_{17}H_{13}FOS$: 284.0668, found: 284.0666.

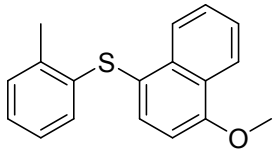


3-((4-Methoxynaphthalen-1-yl)thio)benzonitrile (3ak): Yellow solid, yield: 37.8 mg, 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 6.4, 3.3 Hz, 1H), 8.20 (dd, *J* = 6.3, 3.3 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.55-7.51 (m, 2H), 7.30-7.28 (m, 1H), 7.21-7.20 (m, 2H), 7.14 (s, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 141.8, 136.8, 134.9, 130.1, 129.2,

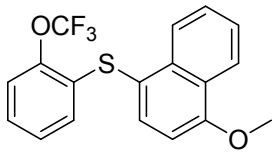
128.8, 128.2, 128.0, 126.7, 126.0, 125.3, 122.9, 118.4, 117.5, 112.9, 104.1, 55.7. HRMS (EI) m/z calcd. for $C_{18}H_{13}NOS$: 297.0715, found: 297.0711.



(4-Methoxynaphthalen-1-yl)(3-(methylsulfonyl)phenyl)sulfane (3al): White solid, yield: 33.1 mg, 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 6.4, 3.3 Hz, 1H), 8.20 (dd, *J* = 6.3, 3.3 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.62-7.57 (m, 2H), 7.52-7.50 (m, 2H), 7.29-7.25 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.05 (s, 3H), 2.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 142.2, 141.0, 136.7, 134.8, 130.7, 129.6, 127.9, 126.7, 125.9, 125.4, 124.3, 123.4, 122.8, 117.6, 104.1, 55.7, 44.2. HRMS (EI) m/z calcd. for $C_{18}H_{16}O_3S_2$: 344.0538, found: 344.0533.

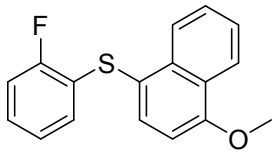


(4-Methoxynaphthalen-1-yl)(*o*-tolyl)sulfane (3am):[1] Yellow oil, yield: 51.0 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.30 (m, 1H), 8.26-8.23 (m, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.50-7.46 (m, 2H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.99-6.96 (m, 1H), 6.87-6.83 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 3.99 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 137.7, 135.1, 135.1, 135.0, 129.9, 127.6, 126.6, 126.5, 126.3, 125.8, 125.7, 124.9, 122.5, 119.9, 104.1, 55.6, 20.1.

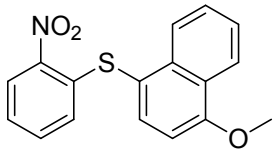


(4-Methoxynaphthalen-1-yl)(2-(trifluoromethoxy)phenyl)sulfane (3an): Yellow solid, yield: 33.6 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35-8.32 (m, 1H), 8.24-8.22 (m, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.51 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.06-7.02 (m, 1H), 6.90-6.83 (m, 2H), 6.45 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 145.0, 137.0, 135.4, 133.4, 127.9, 127.6, 127.0, 126.7, 125.9, 125.8, 125.7, 125.6, 122.7, 120.7, 117.5,

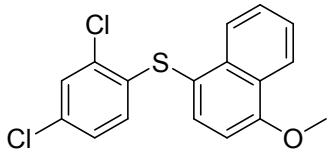
104.2, 55.7. HRMS (EI) m/z calcd. for $C_{18}H_{13}F_3OS$: 334.0636, found: 334.0634.



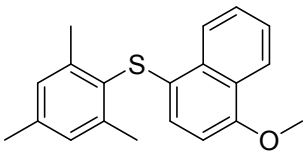
(2-Fluorophenyl)(4-methoxynaphthalen-1-yl)sulfane (3ao):[1] Yellow oil, yield: 47.1 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.29 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.52-7.50 (m, 2H), 7.04-7.01 (m, 2H), 6.83-6.77 (m, 2H), 6.59-6.55 (m, 1H), 4.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, *J* = 242.8 Hz), 157.3, 136.2, 135.2, 128.7(0), 128.6(8), 127.8, 126.5 (d, *J* = 7.6 Hz), 126.2 (d, *J* = 6.9 Hz), 125.7 (d, *J* = 7.6 Hz), 125.6, 124.4 (d, *J* = 3.5 Hz), 122.6, 118.2, 115.20 (d, *J* = 21.3 Hz), 104.1, 55.6.



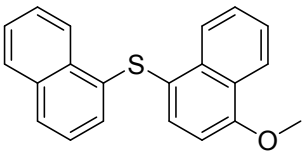
(4-Methoxynaphthalen-1-yl)(2-nitrophenyl)sulfane (3ap): Orange solid, yield: 13.1 mg, 21%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.35 (m, 1H), 8.28-8.26 (m, 1H), 8.15-8.13 (m, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.54-7.51 (m, 2H), 7.16-7.13 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.59-6.57 (m, 1H), 4.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 144.7, 140.0, 137.2, 135.2, 133.4, 128.2, 127.9, 126.7, 126.1, 125.9, 125.4, 124.5, 122.8, 118.1, 104.3, 55.8. HRMS (EI) m/z calcd. for $C_{17}H_{13}NO_3S$: 311.0612, found: 311.0610.



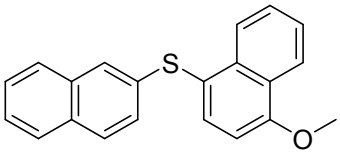
(2,4-Dichlorophenyl)(4-methoxynaphthalen-1-yl)sulfane (3aq): White solid, yield: 56.3 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.32 (m, 1H), 8.18-8.15 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.34 (d, *J* = 2.2 Hz, 1H), 6.83-6.78 (m, 2H), 6.26 (d, *J* = 8.6 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 137.3, 136.9, 135.1, 130.7, 130.5, 129.0, 128.0, 127.5, 127.2, 126.7, 126.0, 125.5, 122.7, 117.6, 104.2, 55.7. HRMS (EI) m/z calcd. for $C_{17}H_{12}Cl_2OS$: 333.9982, found: 333.9981.



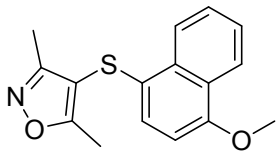
Mesityl(4-methoxynaphthalen-1-yl)sulfane (3ar): Colorless oil, yield: 25.9 mg, 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.3 Hz, 1H), 8.28-8.26 (m, 1H), 7.60-7.56 (m, 1H), 7.53-7.49 (m, 1H), 7.02 (s, 2H), 6.58-6.53 (m, 2H), 3.90 (s, 3H), 2.38 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 143.8, 138.9, 131.7, 129.4, 127.7, 126.5, 126.1, 126.0, 125.4, 124.0, 122.5, 122.2, 104.3, 55.4, 21.7, 21.1. HRMS (EI) m/z calcd. for $C_{20}H_{20}OS$: 308.1231, found: 308.1226.



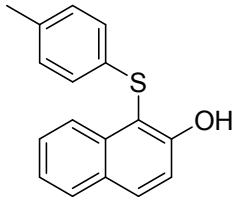
(4-Methoxynaphthalen-1-yl)(naphthalen-1-yl)sulfane (3as): White solid, yield: 33.5 mg, 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.3 Hz, 1H), 8.34-8.29 (m, 2H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.60-7.47 (m, 5H), 7.15-7.11 (m, 1H), 6.81 (t, *J* = 8.5 Hz, 2H), 4.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 135.6, 135.0, 134.8, 133.8, 131.0, 128.5, 127.6, 126.6, 126.2, 125.8, 125.7, 125.1, 124.2 122.6, 120.1, 104.2, 55.6. HRMS (EI) m/z calcd. for $C_{21}H_{16}OS$: 316.0918, found: 316.0911.



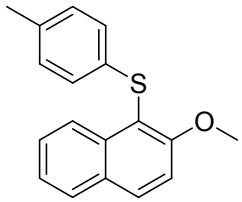
(4-Methoxynaphthalen-1-yl)(naphthalen-2-yl)sulfane (3at): Yellow solid, yield: 51.8 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35-8.31 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.69-7.67 (m, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.50-7.45 (m, 3H), 7.40 (s, 1H), 7.34-7.31 (m, 2H), 7.19 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 136.5, 135.7, 135.1, 133.7, 131.3, 128.3, 127.7, 127.6, 126.9, 126.6, 126.3, 125.9, 125.7, 125.3, 125.2, 124.5, 122.5, 120.0, 104.0, 55.6. HRMS (EI) m/z calcd. for $C_{21}H_{16}OS$: 316.0918, found: 316.0914.



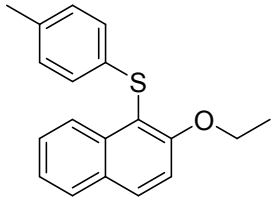
4-((4-Methoxynaphthalen-1-yl)thio)-3,5-dimethylisoxazole (3au): Yellow oil, yield: 43.9 mg, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32-8.28 (m, 2H), 7.61-7.57 (m, 1H), 7.54-7.50 (m, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 3.94 (s, 3H), 2.48 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 162.3, 154.9, 132.4, 127.0, 126.5, 126.1, 125.6, 124.0, 122.8, 122.6, 105.4, 103.9, 55.5, 11.6, 10.3. HRMS (EI) m/z calcd. for $C_{16}H_{15}NO_2S$: 285.0819, found: 285.0812.



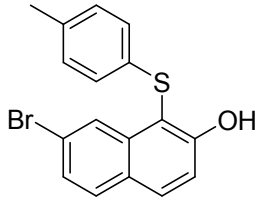
1-(*p*-Tolylthio)naphthalen-2-ol (4aa):[3] Yellow solid, yield: 44.7 mg, 84%; 42.6 mg, 80%; 38.1 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.49-7.45 (m, 1H), 7.36-7.30 (m, 2H), 7.22-7.21 (m, 1H), 6.97-6.92 (m, 4H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 135.8, 135.4, 132.6, 131.7, 129.9, 129.4, 128.5, 127.8, 126.6, 124.7, 123.7, 116.8, 108.7, 20.8.



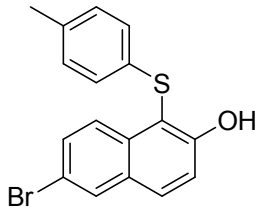
(2-Methoxynaphthalen-1-yl)(*p*-tolyl)sulfane (4ab):[3] Yellow solid, yield: 29.1 mg, 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 9.1 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.50-7.46 (m, 1H), 7.38-7.32 (m, 2H), 6.93 (m, 4H), 3.94 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 136.4, 136.2, 134.5, 131.8, 130.1, 129.5, 129.4, 128.2, 127.6, 126.6, 125.5, 124.0, 113.4, 56.9, 20.8.



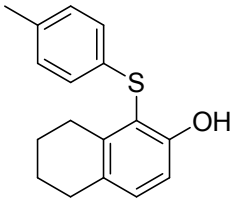
(2-Ethoxynaphthalen-1-yl)(*p*-tolyl)sulfane (4ac):[3] Yellow solid, yield: 44.7 mg, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.50-7.46 (m, 1H), 7.38-7.34 (m, 1H), 7.29 (d, *J* = 9.0 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 4H), 6.93 (d, *J* = 8.1 Hz, 4H), 4.16 (q, *J* = 7.0 Hz, 2H), 2.22 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 136.3, 134.8, 134.6, 131.4, 129.5, 129.3, 128.1, 127.4, 127.2, 125.6, 124.0, 115.0, 65.5, 20.8, 14.8.



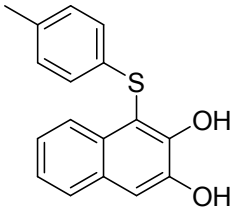
7-Bromo-1-(*p*-tolylthio)naphthalen-2-ol (4ad): White solid, yield: 48.3 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 1.7 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.42 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.24 (s, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 136.8, 136.2, 132.5, 131.1, 130.1, 130.0, 127.8, 127.3, 127.0, 126.7, 122.7, 117.2, 108.2, 20.9. HRMS (EI) m/z calcd. for $C_{16}H_{15}NO_2S$: 285.0819, found: 285.0812.



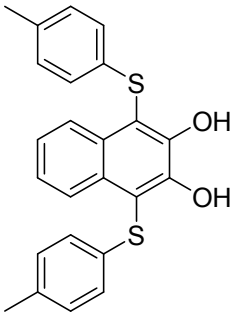
6-Bromo-1-(*p*-tolylthio)naphthalen-2-ol (4ae):[3] White solid, yield: 53.8 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.53 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 7.21 (s, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 136.2, 134.0, 131.5, 131.3, 131.0, 130.5, 130.4, 130.0, 126.7(2), 126.6(7), 118.0, 117.6, 109.2, 20.9.



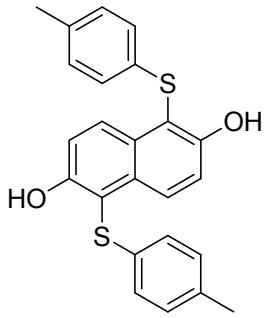
1-(*p*-Tolylthio)-5,6,7,8-tetrahydronaphthalen-2-ol (4af):[3] White solid, yield: 11.4 mg, 21%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.92-6.87 (m, 3H), 6.76 (s, 1H), 2.77-2.71 (m, 4H), 2.27 (s, 3H), 1.72-1.70 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 142.0, 135.6, 132.6, 131.7, 130.0, 129.9, 126.3, 115.4, 112.2, 29.3, 28.2, 23.1, 22.7, 20.9.



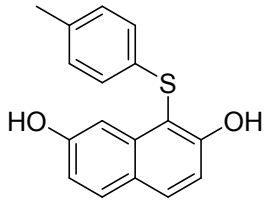
1-(*p*-Tolylthio)naphthalene-2,3-diol (4ag): Yellow solid, yield: 26.0 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.11 (m, 1H), 7.72-7.69 (m, 1H), 7.42 (s, 1H), 7.36-7.34 (m, 2H), 7.25-7.24 (m, 1H), 7.01-6.93 (m, 4H), 5.77 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 144.0, 136.1, 131.3, 130.0(3), 130.0(1), 129.9, 127.3, 127.2, 126.8, 125.3, 124.7, 112.9, 109.4, 20.9. HRMS (EI) m/z calcd. for $C_{17}H_{14}O_2S$: 282.0712, found: 282.0707.



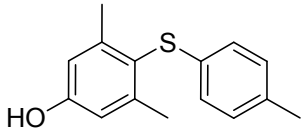
1,4-Bis(*p*-tolylthio)naphthalene-2,3-diol (4ah): Yellow solid, yield: 13.0 mg, 16%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.39 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.21 (s, 2H), 7.04-6.99 (m, 8H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 136.3, 131.1, 130.4, 130.0, 127.3, 125.8, 125.4, 113.5, 20.9. HRMS (EI) m/z calcd. for $C_{24}H_{20}O_2S_2$: 404.0901, found: 404.0895.



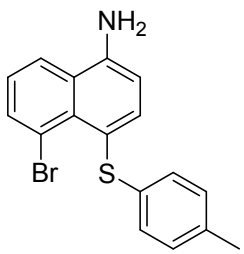
1,5-Bis(*p*-tolylthio)naphthalene-2,6-diol (4ai): Yellow solid, yield: 16.2 mg, 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9.2 Hz, 2H), 7.33 (d, *J* = 9.2 Hz, 2H), 7.02-6.94 (m, 10H), 2.23 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 136.1, 131.6, 131.2, 130.0, 129.3, 126.7, 118.4, 109.9, 20.9. HRMS (EI) m/z calcd. for $C_{24}H_{20}O_2S_2$: 404.0901, found: 404.0899.



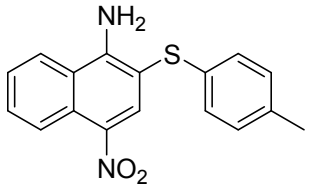
1-(*p*-Tolylthio)naphthalene-2,7-diol (4aj):[3] Yellow solid, yield: 39.5 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.20-7.14 (m, 2H), 6.97-6.90 (m, 5H), 5.37 (s, 1H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 155.4, 137.2, 135.8, 132.5, 131.5, 130.7, 129.9, 126.4, 124.7, 115.2, 114.2, 107.2, 107.0, 20.8.



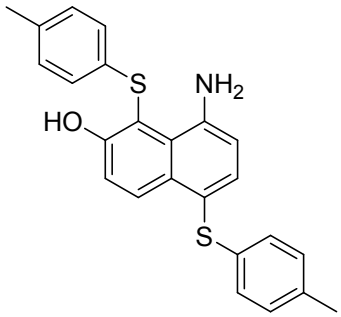
3,5-Dimethyl-4-(*p*-tolylthio)phenol (4ak):[4] White solid, yield: 30.3mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.2 Hz, 2H), 6.67 (s, 2H), 5.20 (s, 1H), 2.36 (s, 6H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 145.8, 134.9, 134.2, 129.6, 125.3, 122.0, 115.3, 21.9, 20.8.



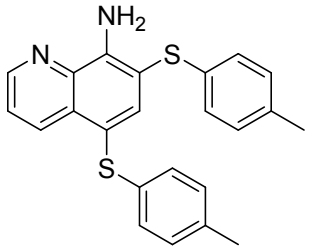
5-Bromo-4-(*p*-tolylthio)naphthalen-1-amine (6aa): Brown solid, yield: 45.4 mg, 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.77 (m, 2H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.31-7.27 (m, 1H), 7.04-6.99 (m, 4H), 4.98 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 135.7, 134.7, 133.3, 132.7, 131.0, 129.8, 127.2, 125.4, 124.3, 123.7, 121.4, 117.5, 110.7, 20.9. HRMS (EI) m/z calcd. for $C_{17}H_{14}BrNS$: 343.0026, found: 343.0020.



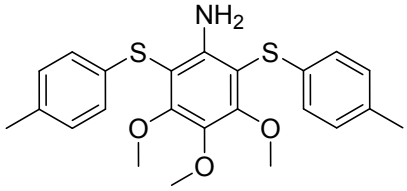
4-Nitro-2-(*p*-tolylthio)naphthalen-1-amine (6ab): Brown solid, yield: 48.4 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 8.8 Hz, 1H), 8.64 (s, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.76-7.72 (m, 1H), 7.59-7.55 (m, 1H), 7.05 (s, 4H), 5.82 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 136.5, 135.9, 135.1, 131.3, 130.5, 130.1, 127.8, 127.5, 126.5, 124.8, 121.8, 121.5, 107.2, 20.9. HRMS (EI) m/z calcd. for $C_{17}H_{14}N_2O_2S$: 310.0773, found: 310.0768.



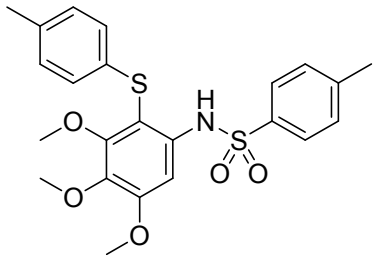
8-Amino-1,5-bis(*p*-tolylthio)naphthalen-2-ol (6ac): Brown solid, yield: 36.3 mg, 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.33-7.25 (m, 5H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 2.29 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 143.4, 137.3, 136.0, 134.6, 132.7, 131.2, 130.5, 129.7, 129.1, 127.4, 126.8, 126.4, 125.7, 124.0, 120.8, 117.0, 104.1, 21.4, 20.9. HRMS (EI) m/z calcd. for $C_{24}H_{21}NOS_2$: 403.1061, found: 403.1054.



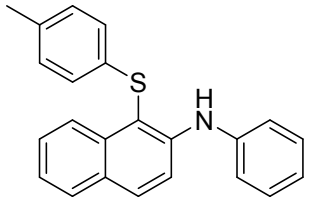
5,7-Bis(*p*-tolylthio)quinolin-8-amine (6ad):[5] Yellow solid, yield: 40.4 mg, 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74-8.73 (m, 1H), 8.59-8.56 (m, 1H), 7.94 (s, 1H), 7.40 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.06 (dd, *J* = 17.6, 8.2 Hz, 4H), 6.95 (dd, *J* = 14.9, 8.4 Hz, 4H), 5.96 (s, 2H), 2.28 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 147.8, 143.3, 138.8, 135.8, 135.2, 135.1, 134.7, 132.3, 130.7, 129.9, 129.6, 127.5, 126.7, 122.9, 114.6, 109.5, 20.9, 20.8.



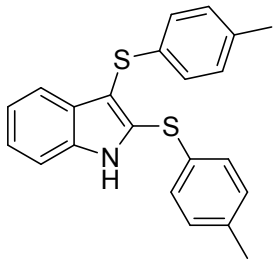
3,4,5-Trimethoxy-2,6-bis(*p*-tolylthio)aniline (6ae): Yellow solid, yield: 37.6 mg, 44%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (dd, *J* = 15.8, 8.3 Hz, 8H), 3.86 (s, 6H), 3.83 (s, 3H), 2.27 (s, 6H). ^{13}C NMR (1010 MHz, $CDCl_3$) δ 158.4, 149.3, 138.0, 135.2, 133.0, 129.7, 126.2, 103.9, 61.6, 61.3, 20.9. HRMS (EI) m/z calcd. for $C_{23}H_{25}NO_3S_2$: 427.1273, found: 427.1268.



4-Methyl-*N*-(3,4,5-trimethoxy-2-(*p*-tolylthio)phenyl)benzenesulfonamide (6af): White solid, yield: 23.0 mg, 25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.19 (s, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 3.79 (s, 3H), 3.67 (s, 3H), 2.36 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 155.5, 143.9, 139.2, 136.2, 135.6, 135.5, 132.5, 129.7, 129.5, 127.2, 126.4, 107.2, 99.0, 61.4, 61.0, 56.1, 21.5, 20.9. HRMS (EI) m/z calcd. for $C_{23}H_{25}NO_5S_2$: 459.1168, found: 459.1166.



***N*-Phenyl-1-(*p*-tolylthio)naphthalen-2-amine (6ag)**: Brown solid, yield: 34.1 mg, 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.5 Hz, 1H), 7.78-7.71 (m, 2H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 (s, 1H), 7.31-7.26 (m, 3H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.06-7.02 (m, 1H), 6.96-6.94 (m, 4H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 141.6, 138.2, 136.5, 135.1, 132.9, 131.3, 129.8, 129.3, 128.3, 127.7, 126.1, 124.8, 123.2, 123.1, 121.3, 116.4, 108.6, 20.8. HRMS (EI) m/z calcd. for $C_{23}H_{19}NS$: 341.1234, found: 341.1230.



2,3-Bis(*p*-tolylthio)-1*H*-indole (6ah):[6] Colorless oil, yield: 33.2 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.27-7.18 (m, 4H), 7.14-7.02 (m, 5H), 6.95 (d, *J* = 8.1 Hz, 2H), 2.30 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.7, 134.8, 134.6, 134.4, 130.7, 130.2, 130.1, 130.0, 129.4, 126.9, 123.4, 121.0, 119.7, 110.9, 108.2, 21.0, 20.9.

4. References

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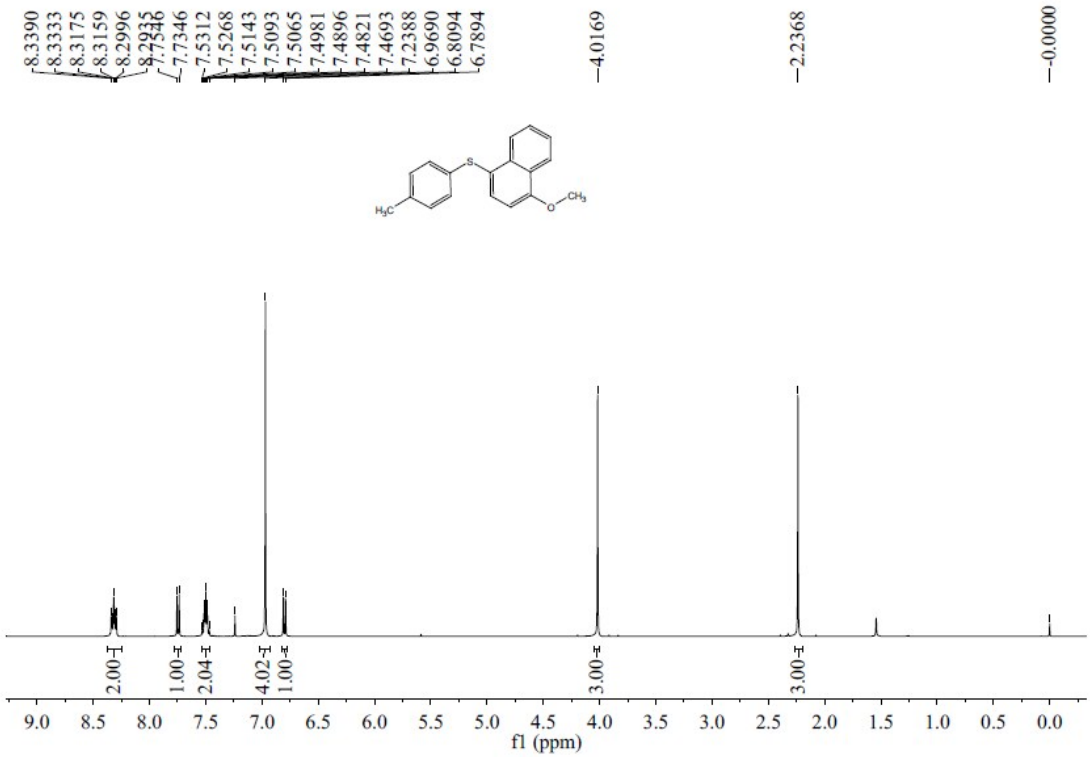
3. X. Kang, R. Yan, G. Yu, X. Pang, X. Liu, X. Li, L. Xiang and G. Huang, *J. Org. Chem.*, 2014, **79**, 10605.

4. D. Wang, S. Guo, R. Zhang, S. Lin and Z. Yan, *RSC Adv.*, 2016, **6**, 54377.

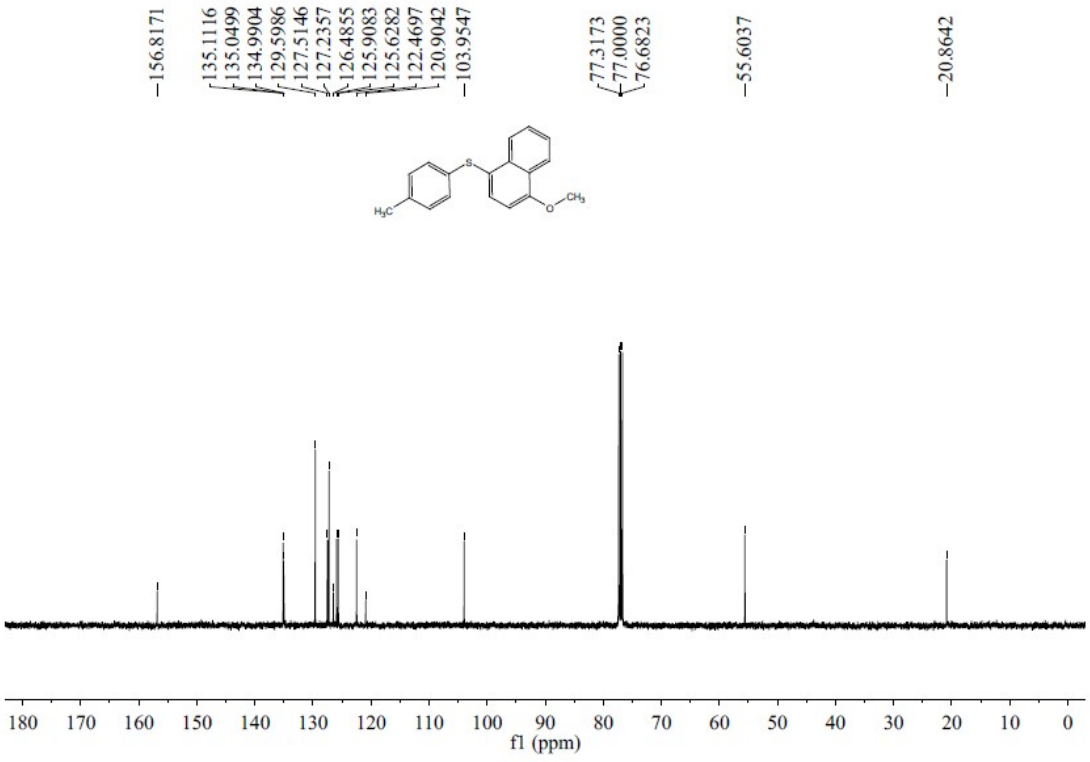
5. Y. Lin, G. Lu, G. Wang and W. Yi, *Adv. Synth. Catal.*, 2016, **358**, 4100.

6. L. Chen, P. Liu, J. Wu and B. Dai, *Tetrahedron*, 2018, **74**, 1513.

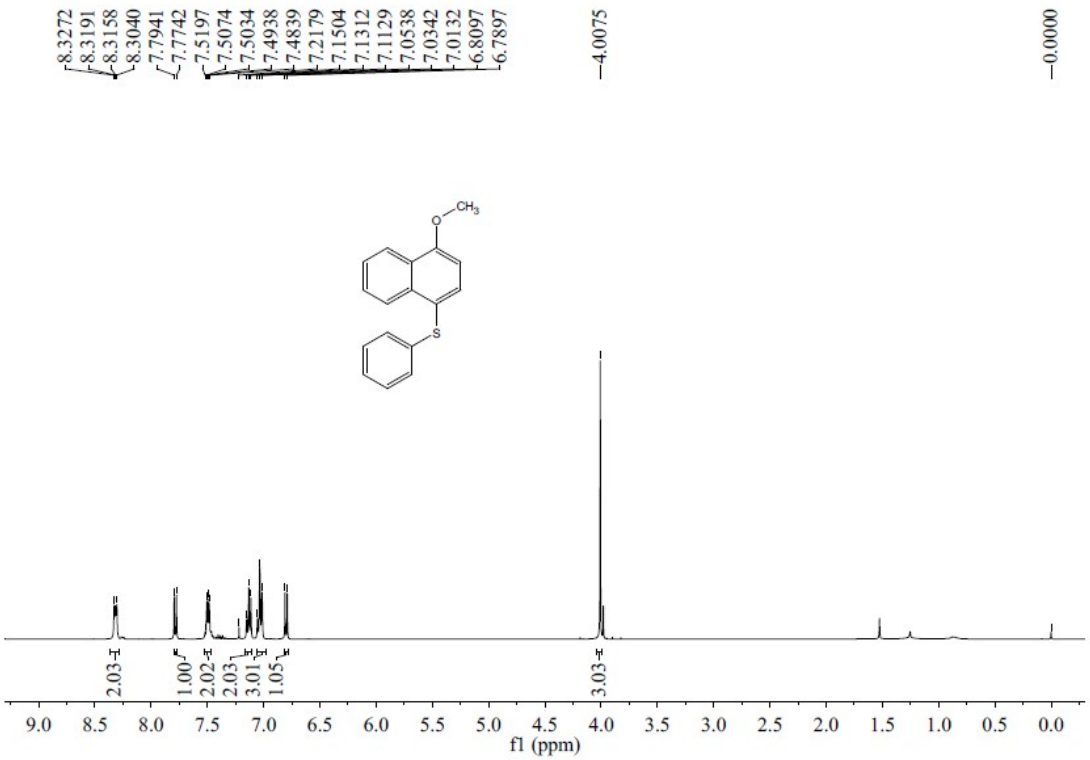
5. ^{1}H and ^{13}C NMR spectra of products



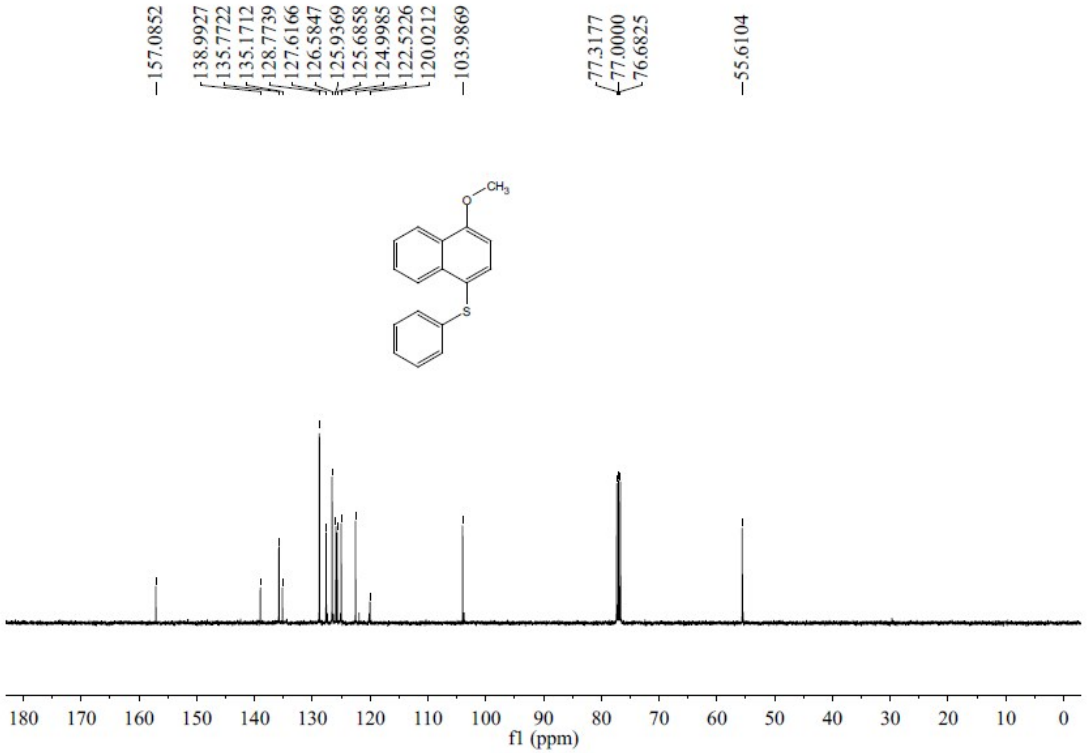
^{1}H NMR of **3aa**



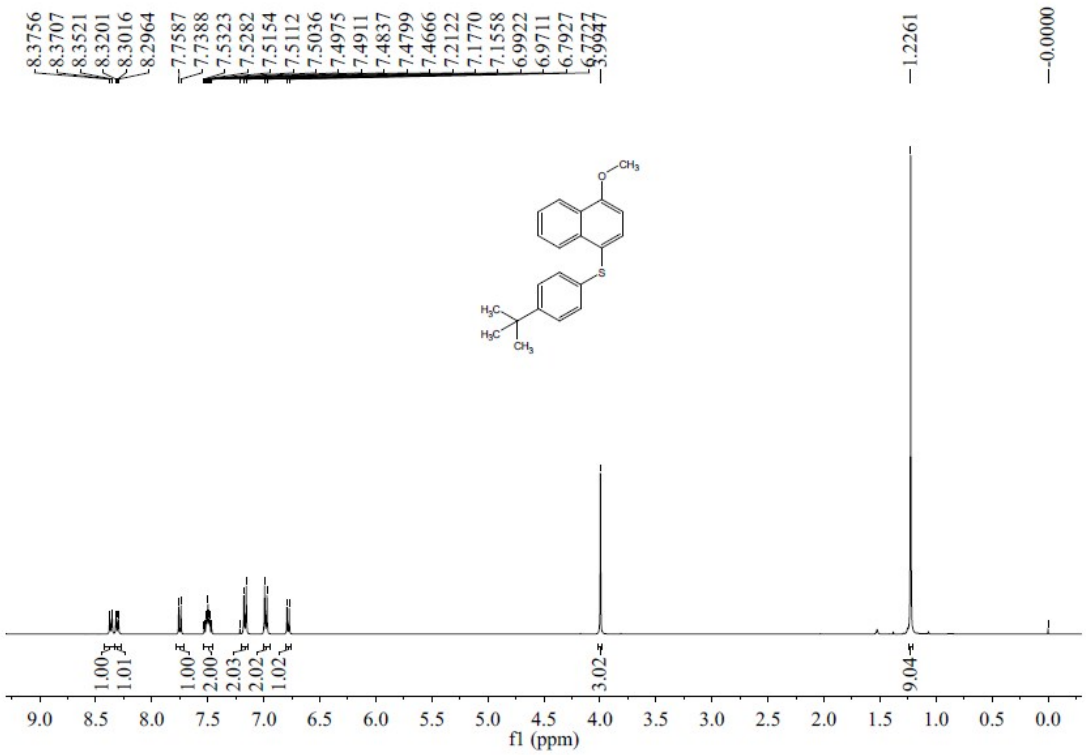
^{13}C NMR of **3aa**



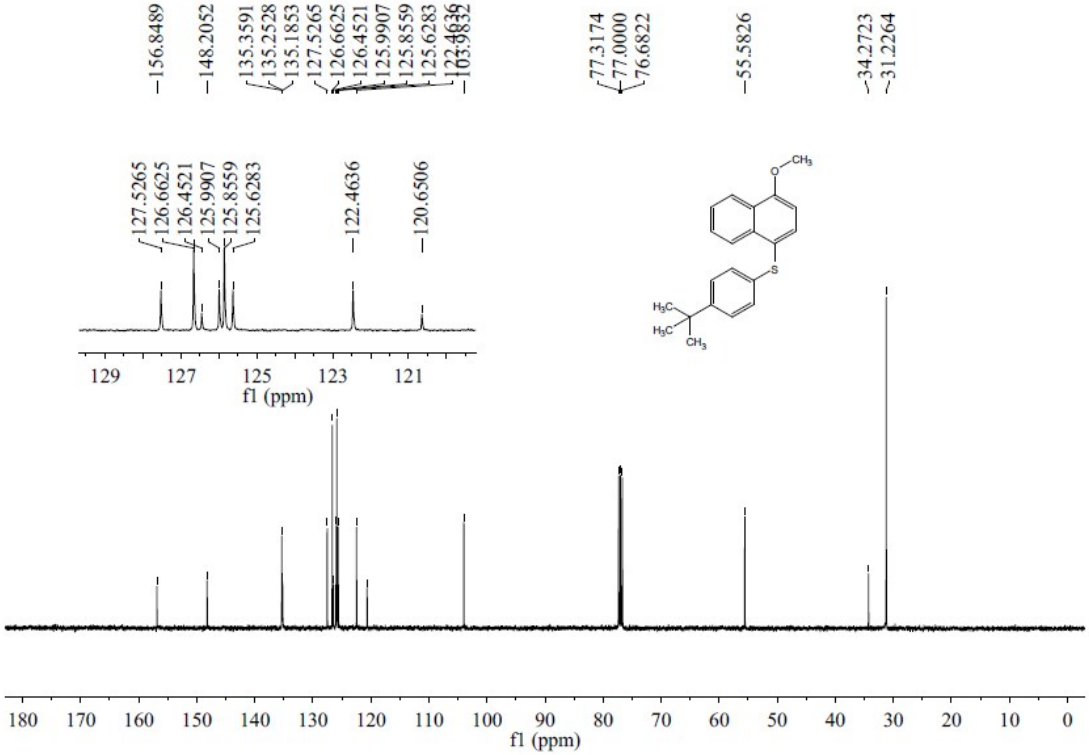
^{1}H NMR of **3ab**



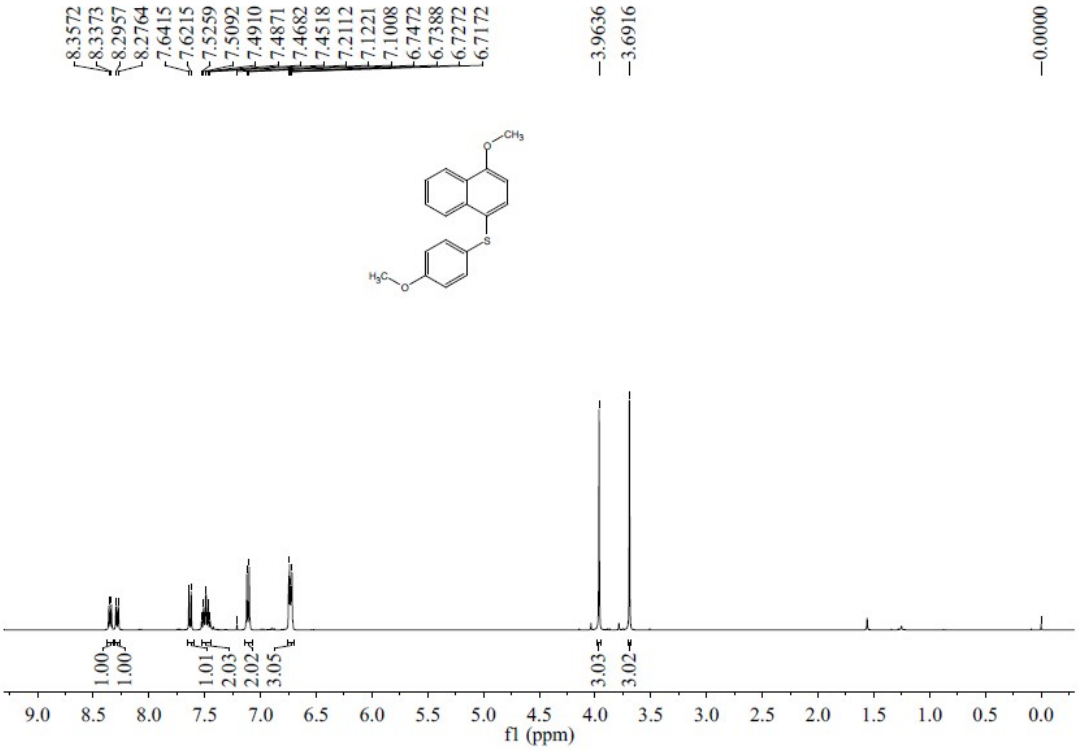
^{13}C NMR of **3ab**



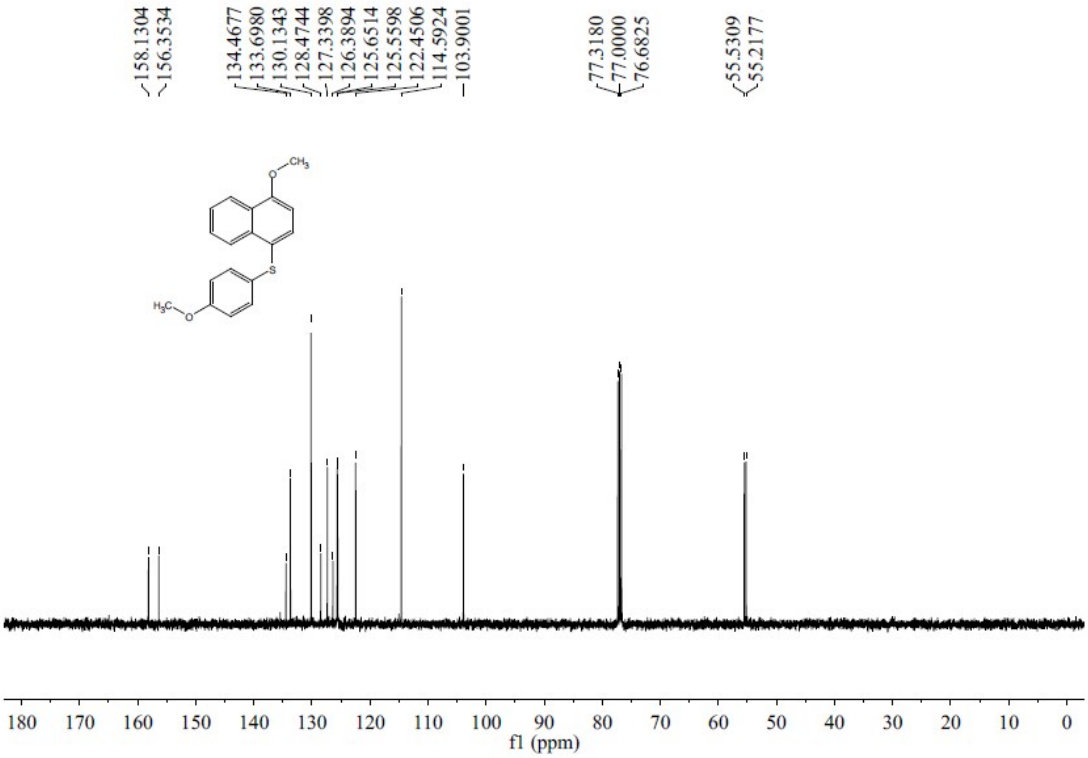
^{1}H NMR of **3ac**



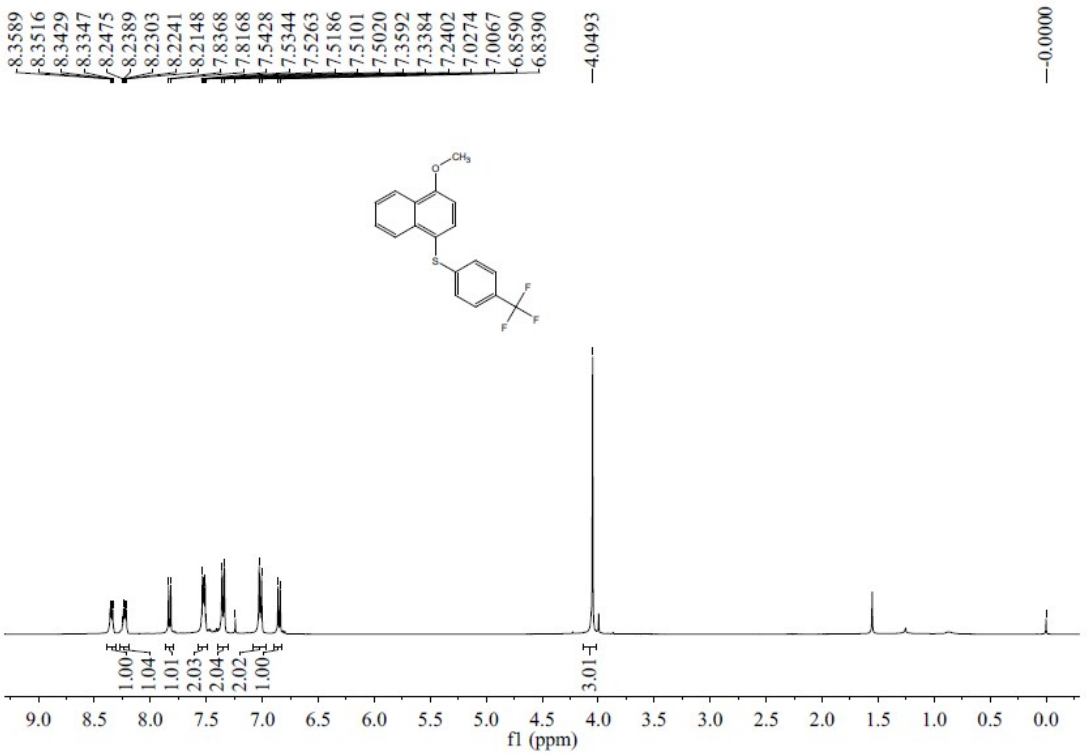
^{13}C NMR of **3ac**



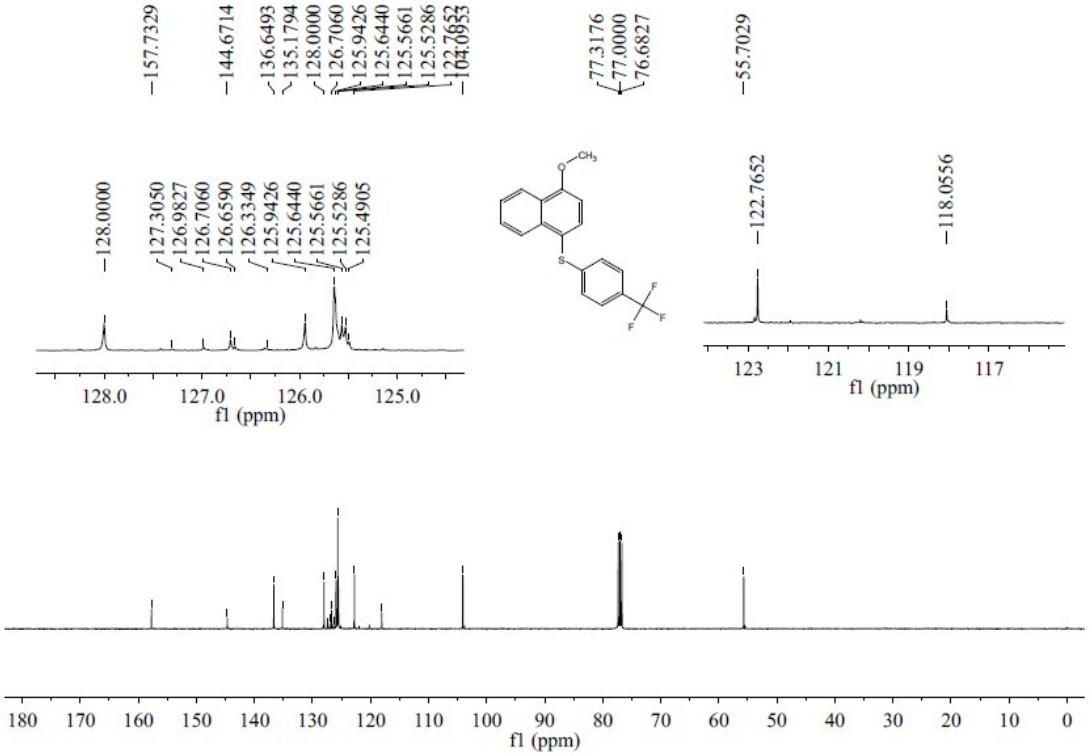
^{1}H NMR of **3ad**



^{13}C NMR of **3ad**



^{1}H NMR of **3ae**



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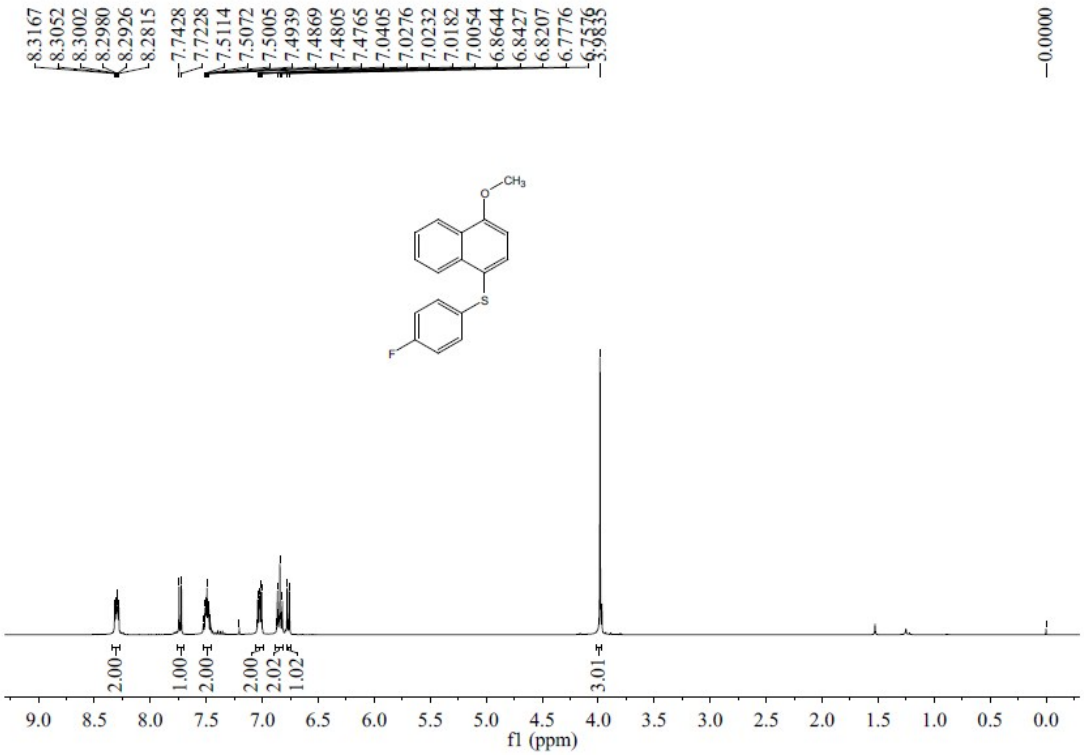
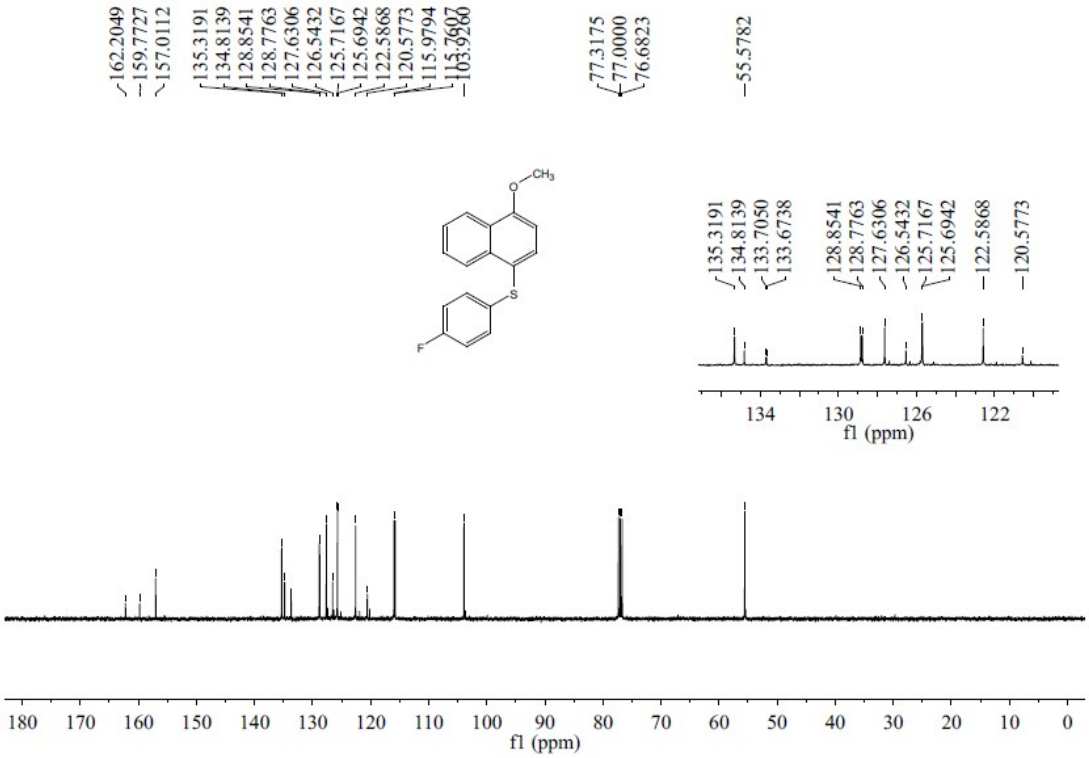
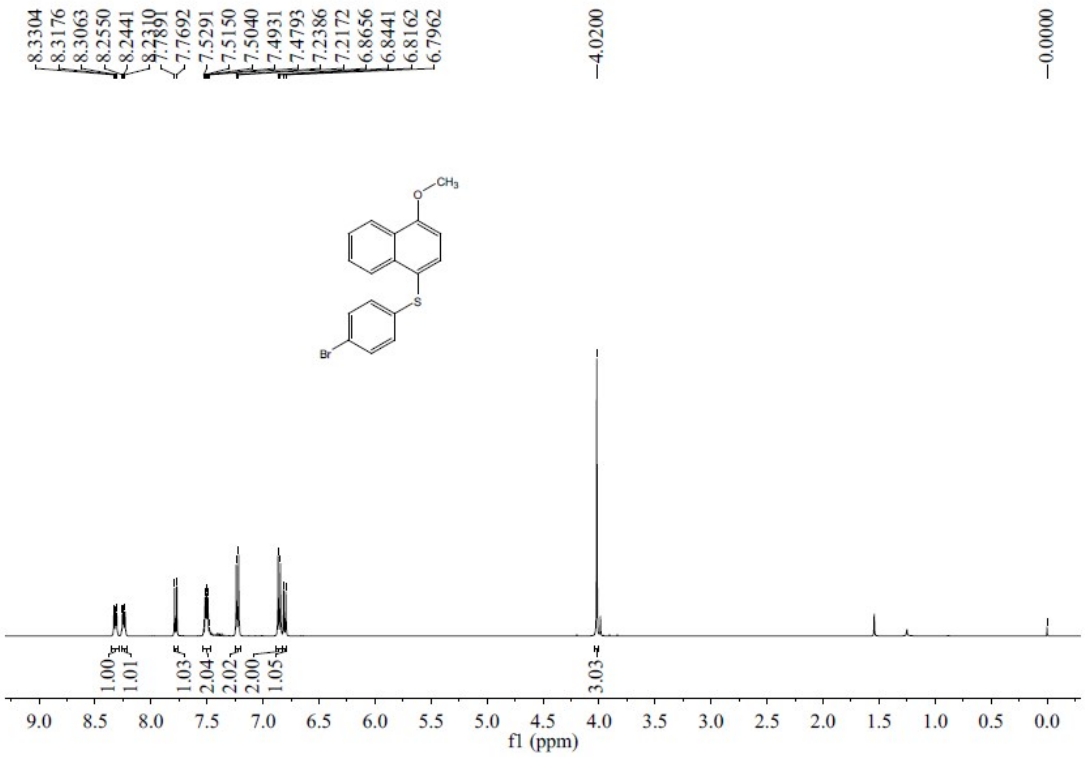


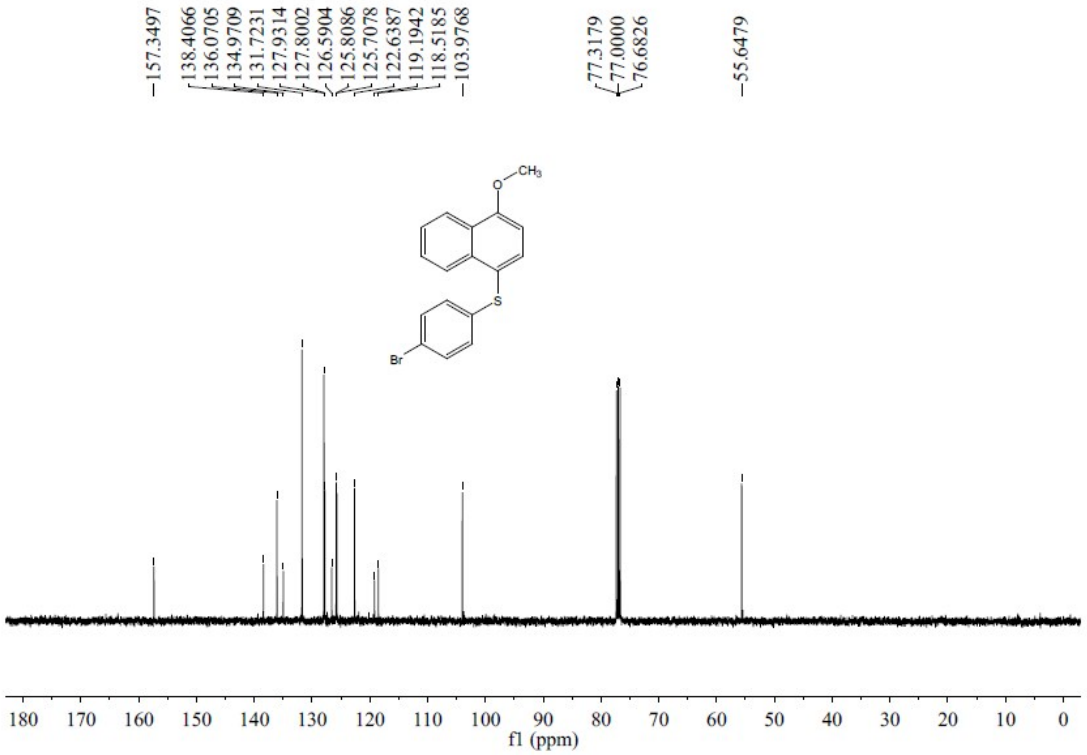
^{1}H NMR of **3af**



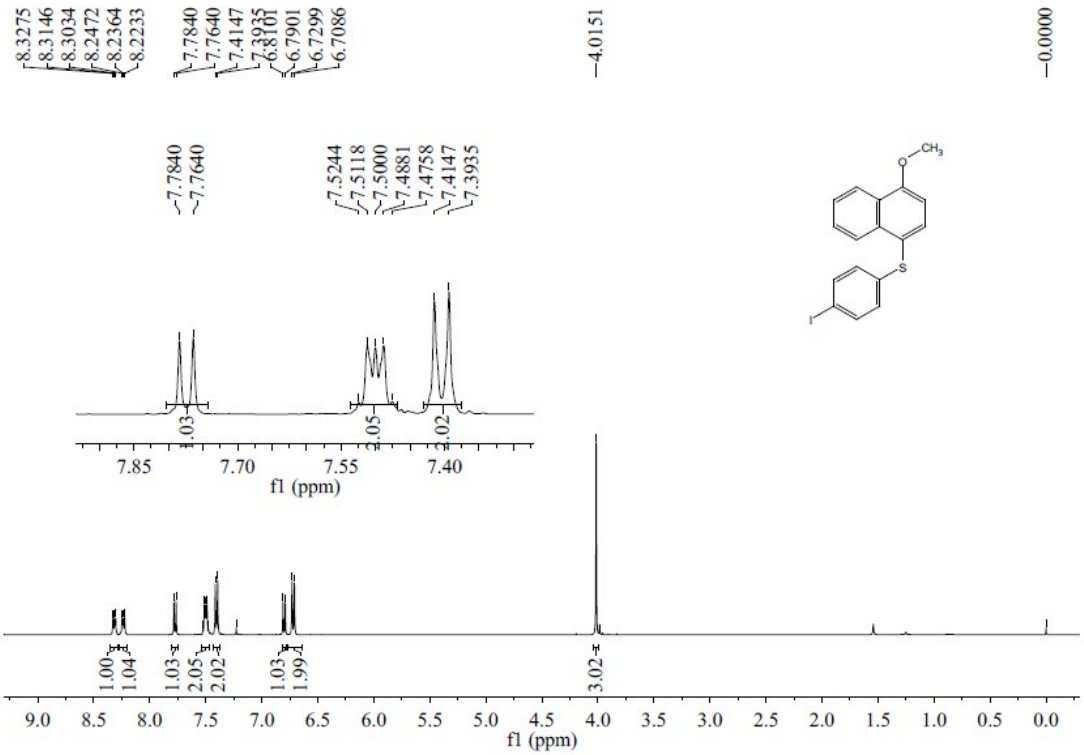
^{13}C NMR of **3af**



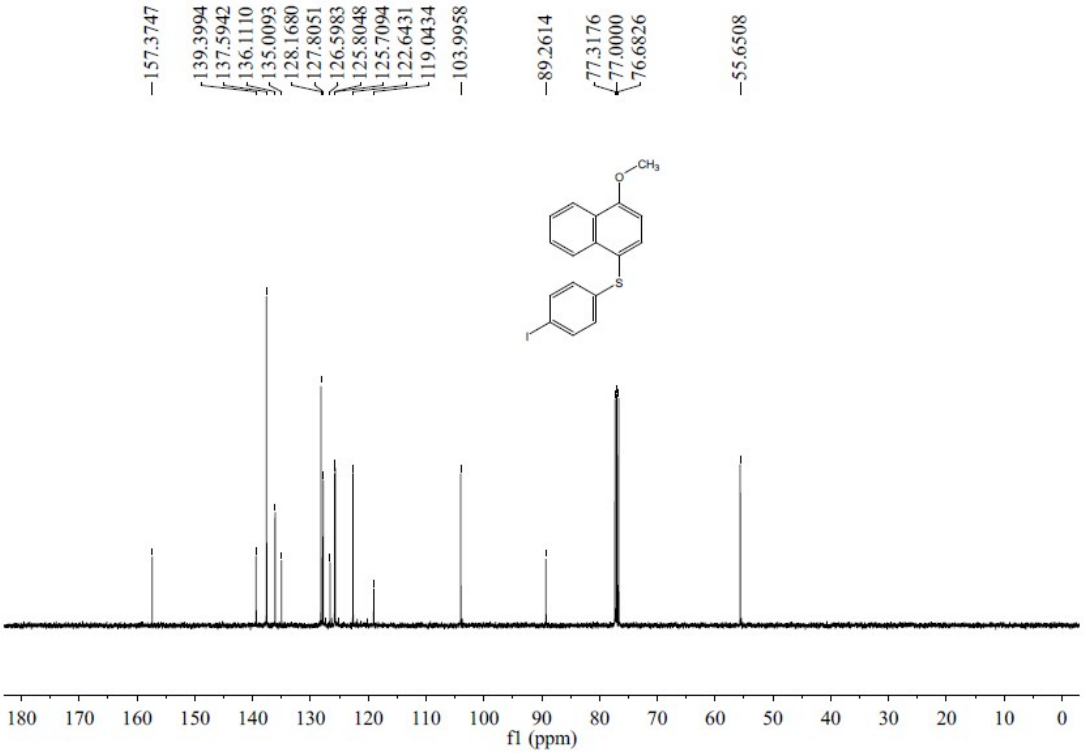
^{1}H NMR of **3ag**



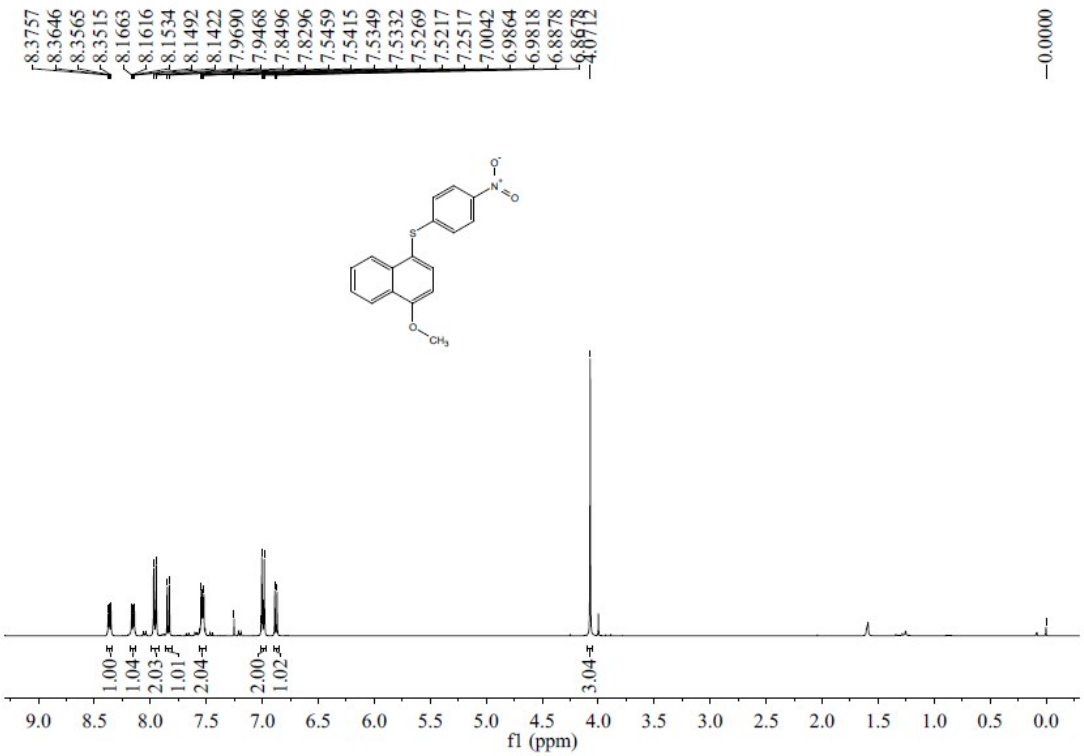
^{13}C NMR of **3ag**



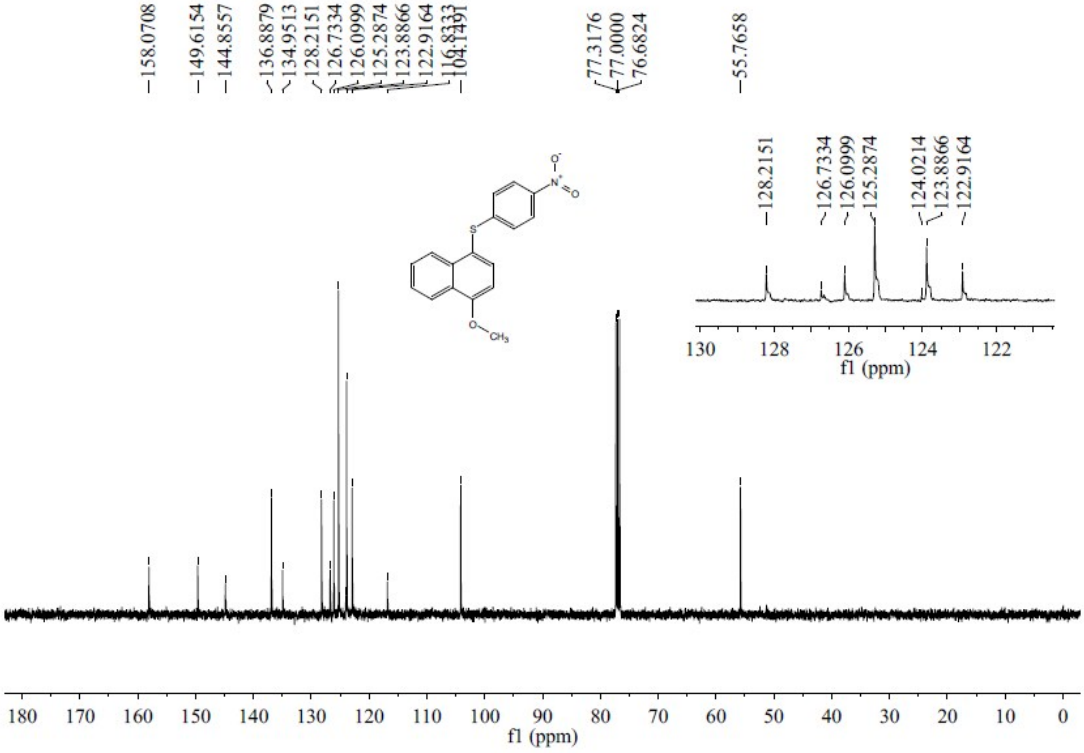
^{1}H NMR of **3ah**



^{13}C NMR of **3ah**



^{1}H NMR of **3ai**



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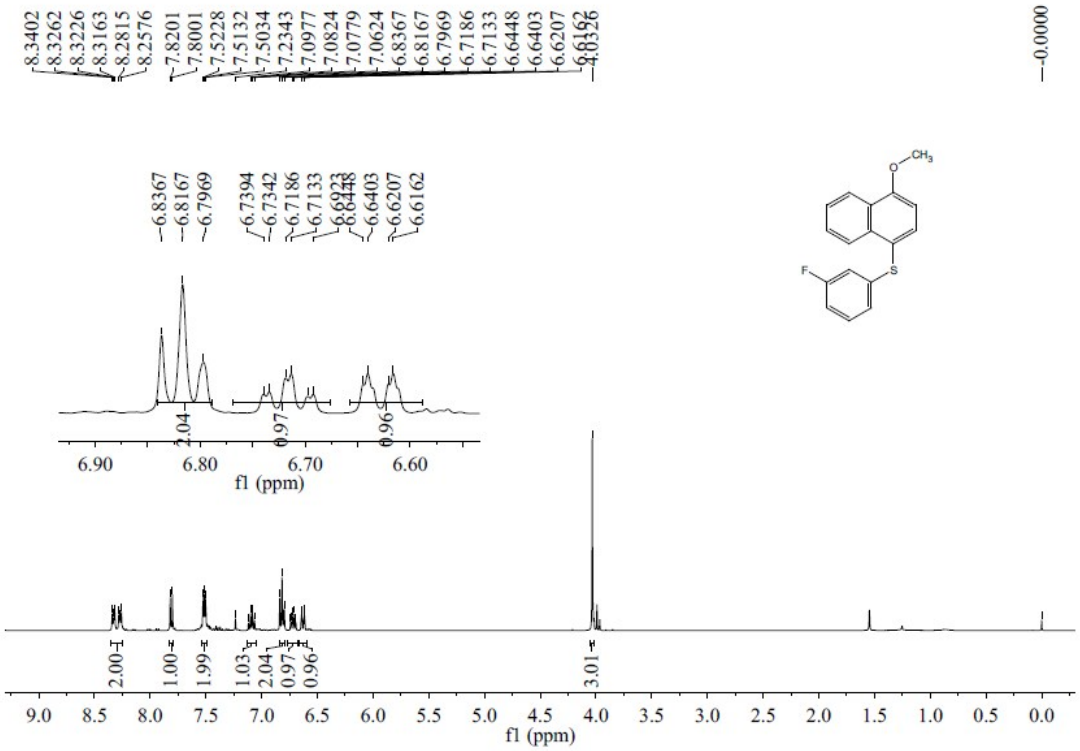
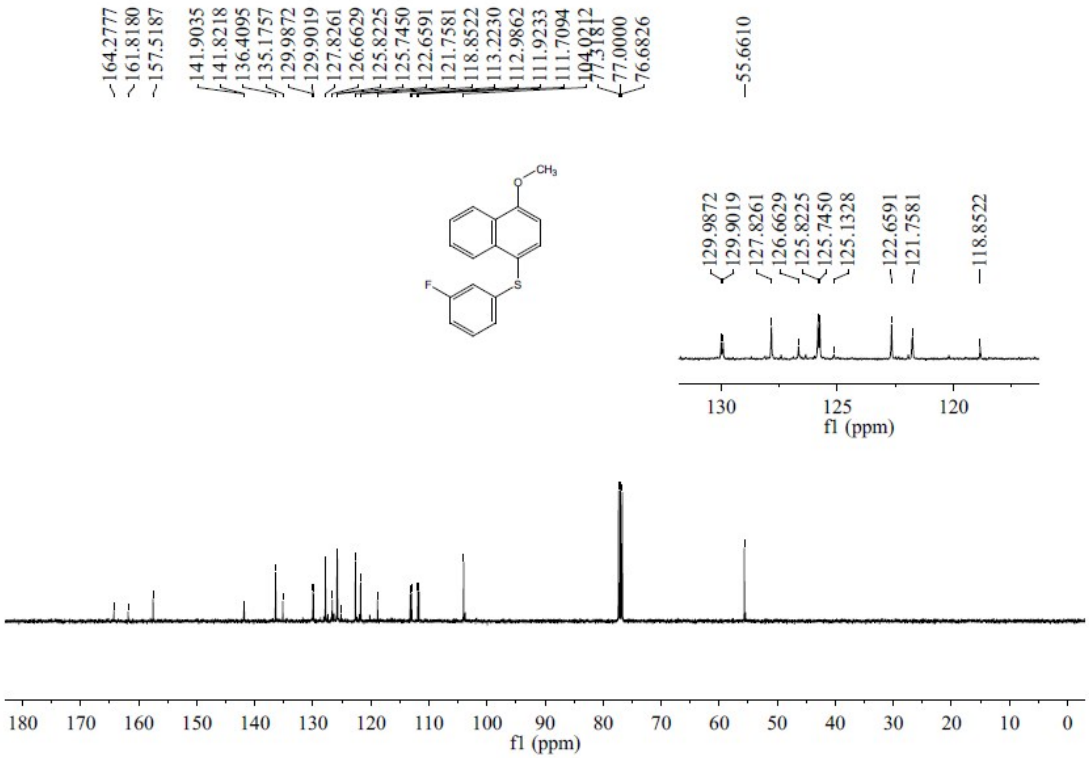
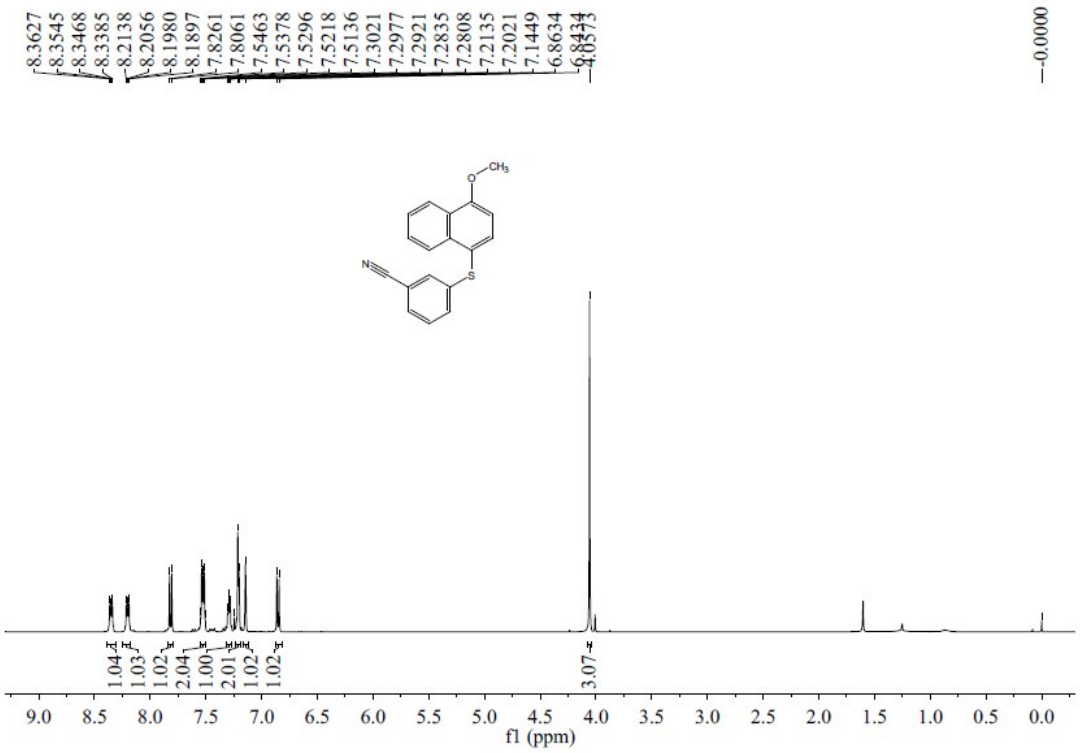


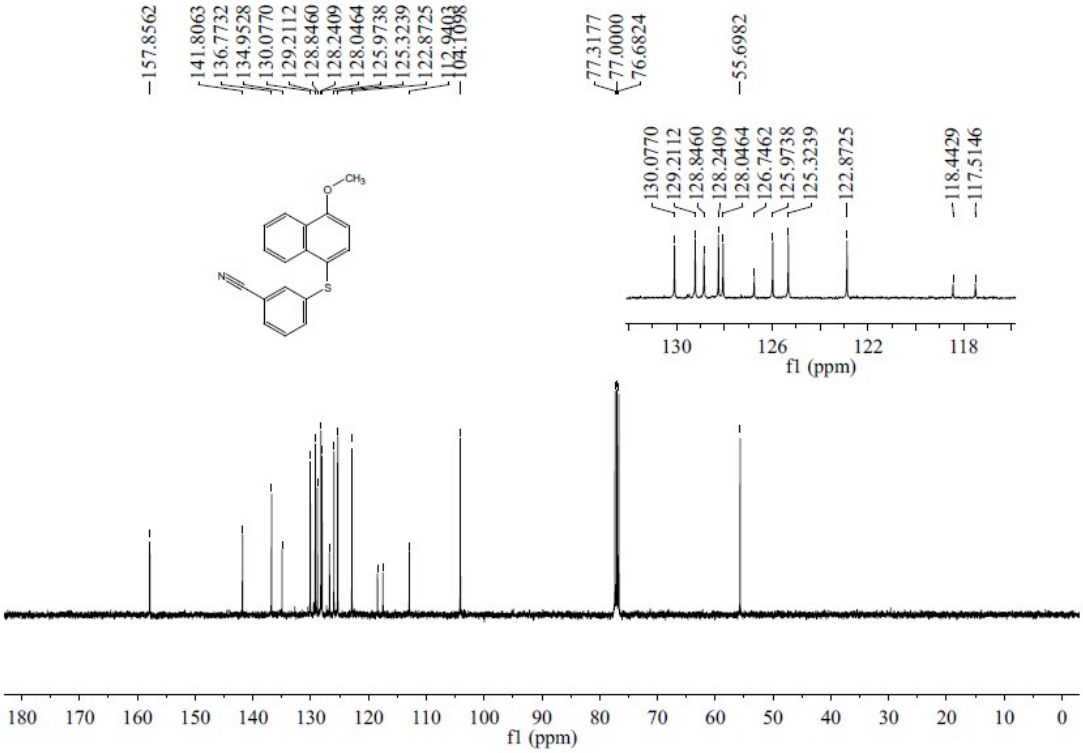
^{1}H NMR of **3aj**



^{13}C NMR of **3aj**



^{1}H NMR of **3ak**



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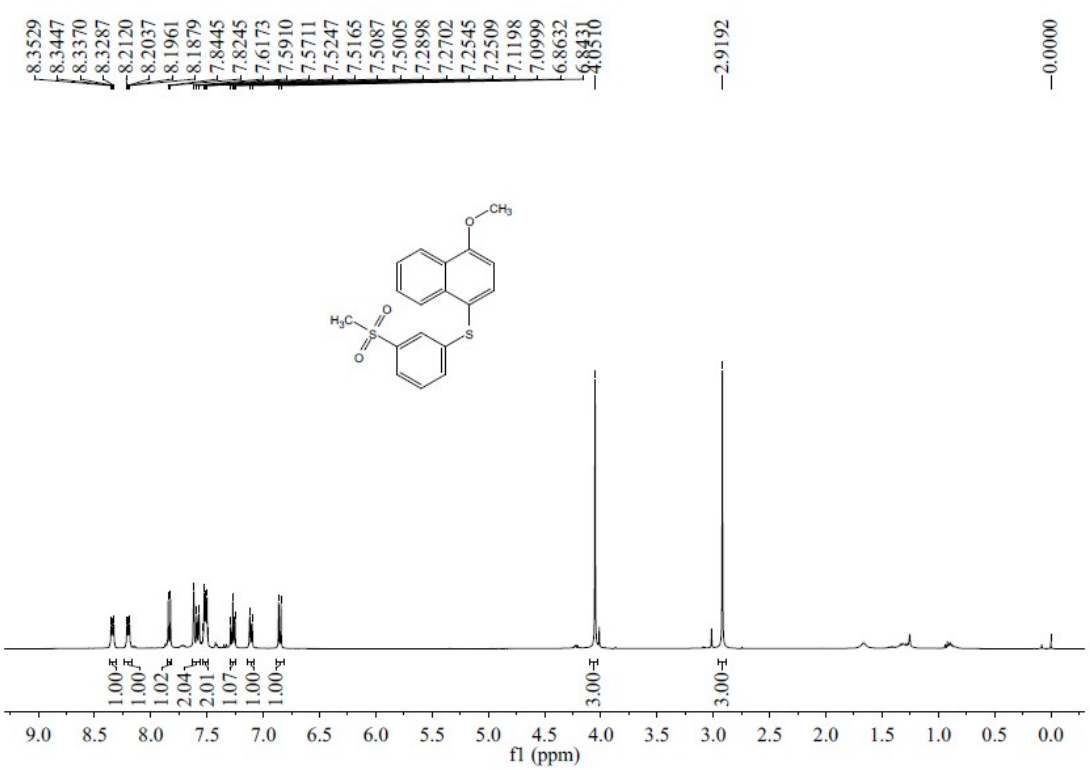
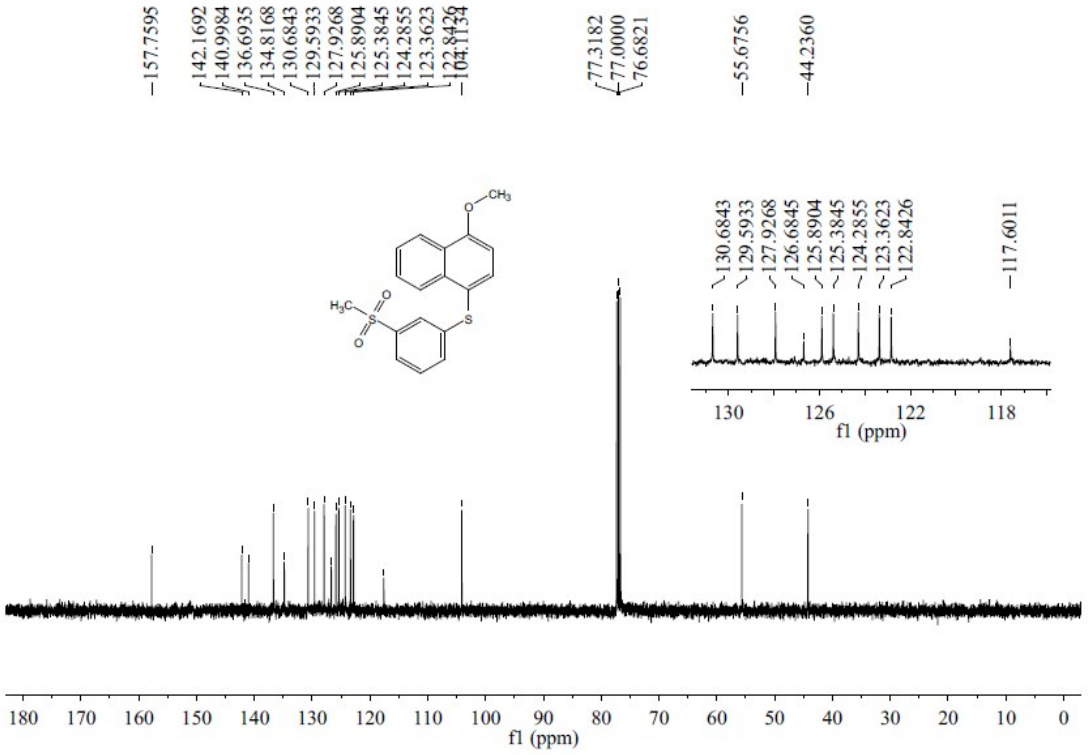
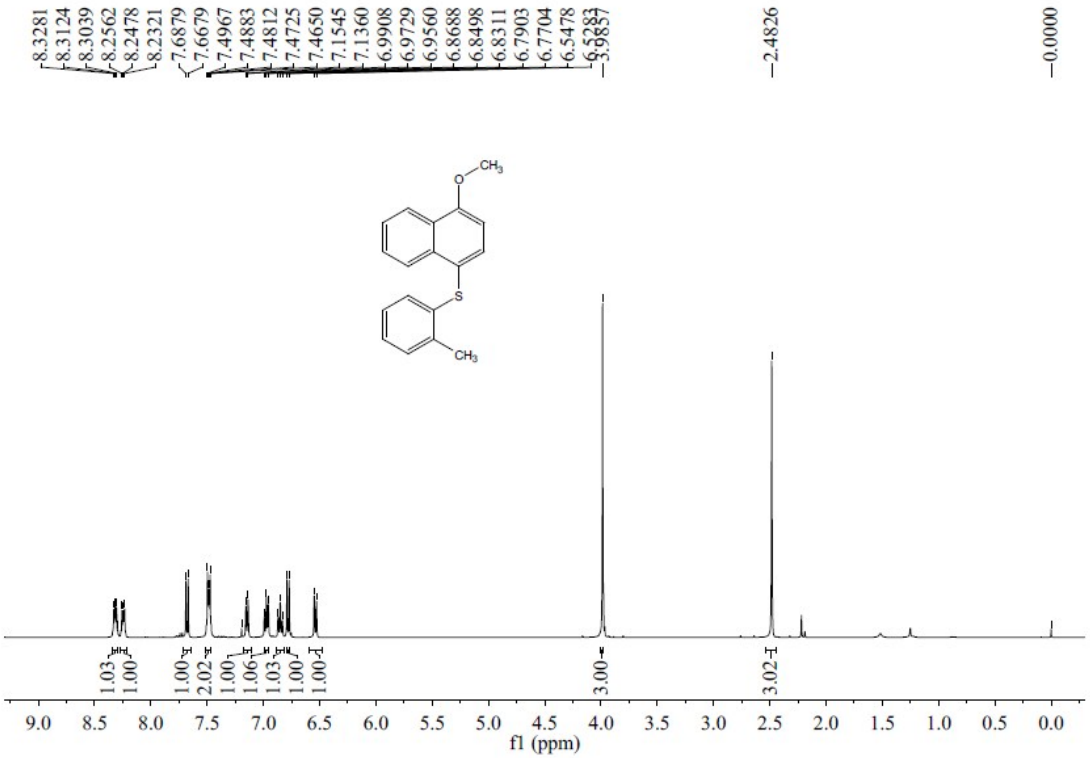


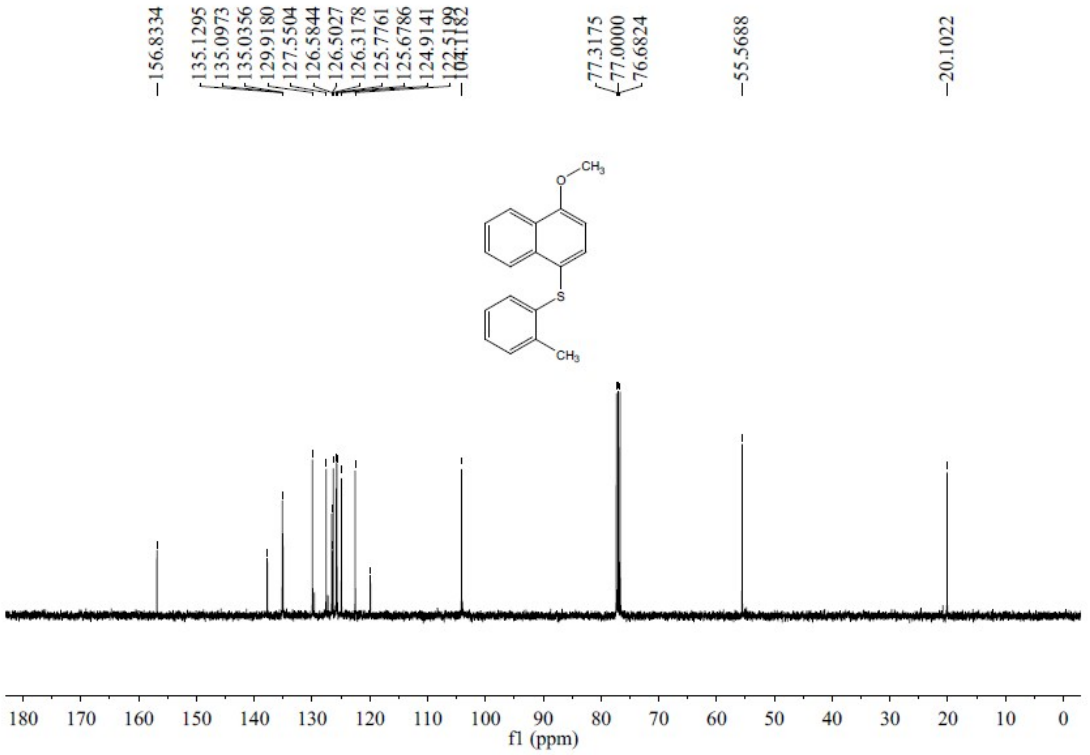
^{1}H NMR of **3al**



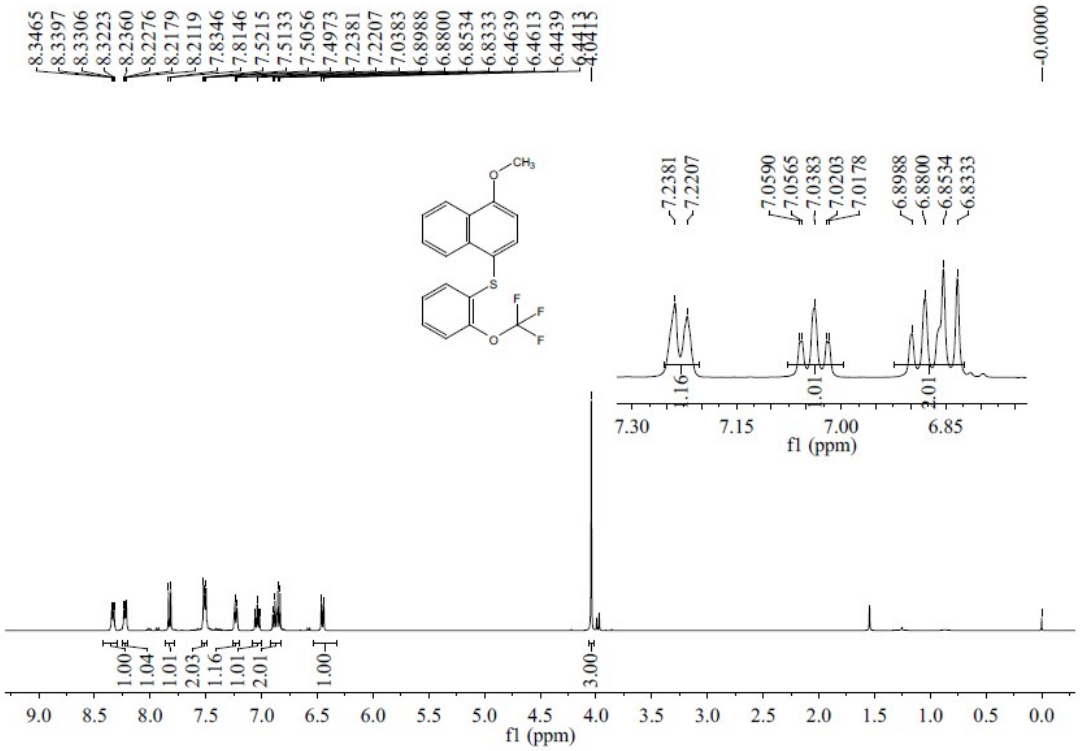
^{13}C NMR of **3al**



^{1}H NMR of **3am**



^{13}C NMR of **3am**



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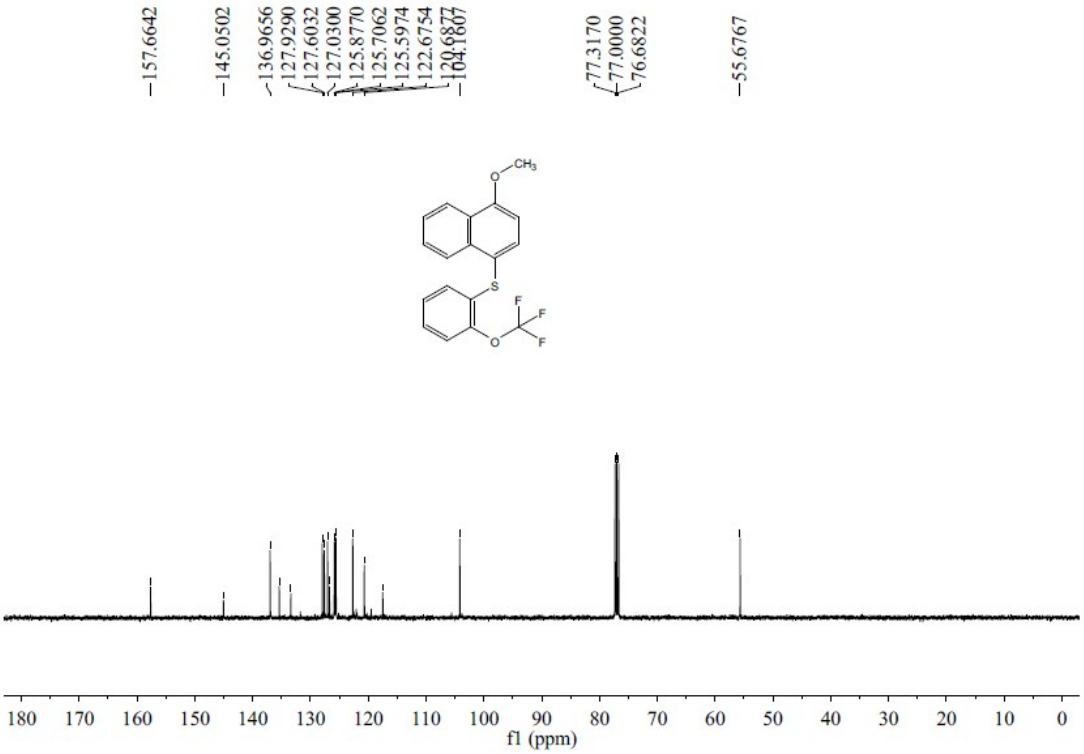
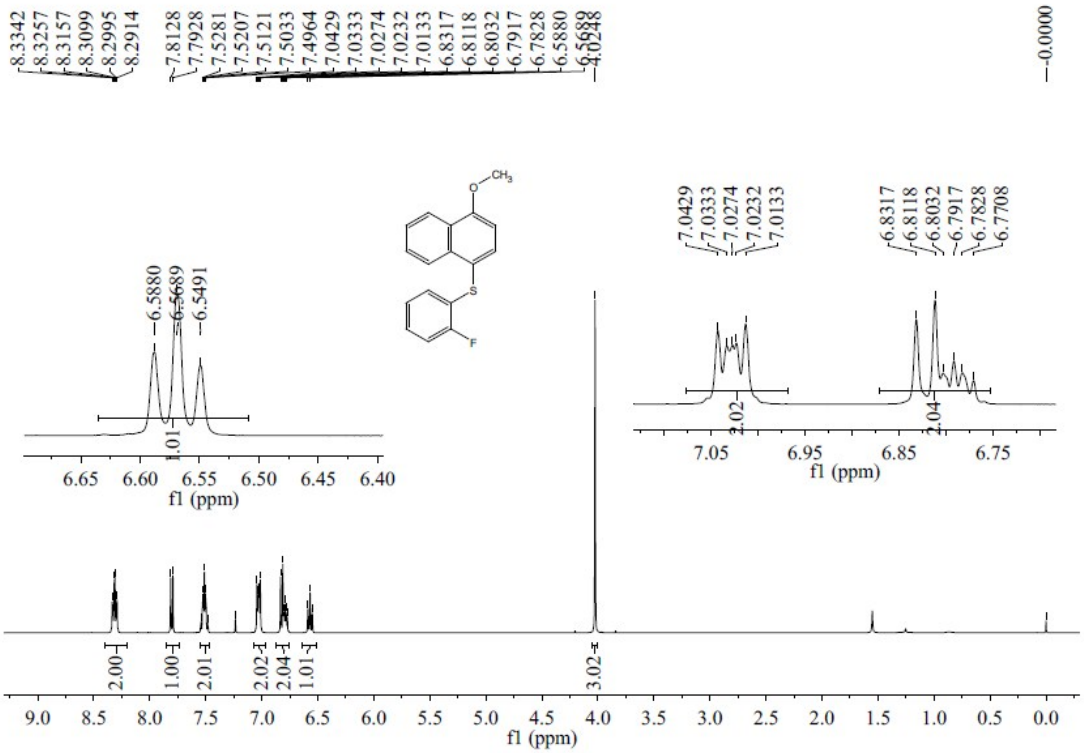
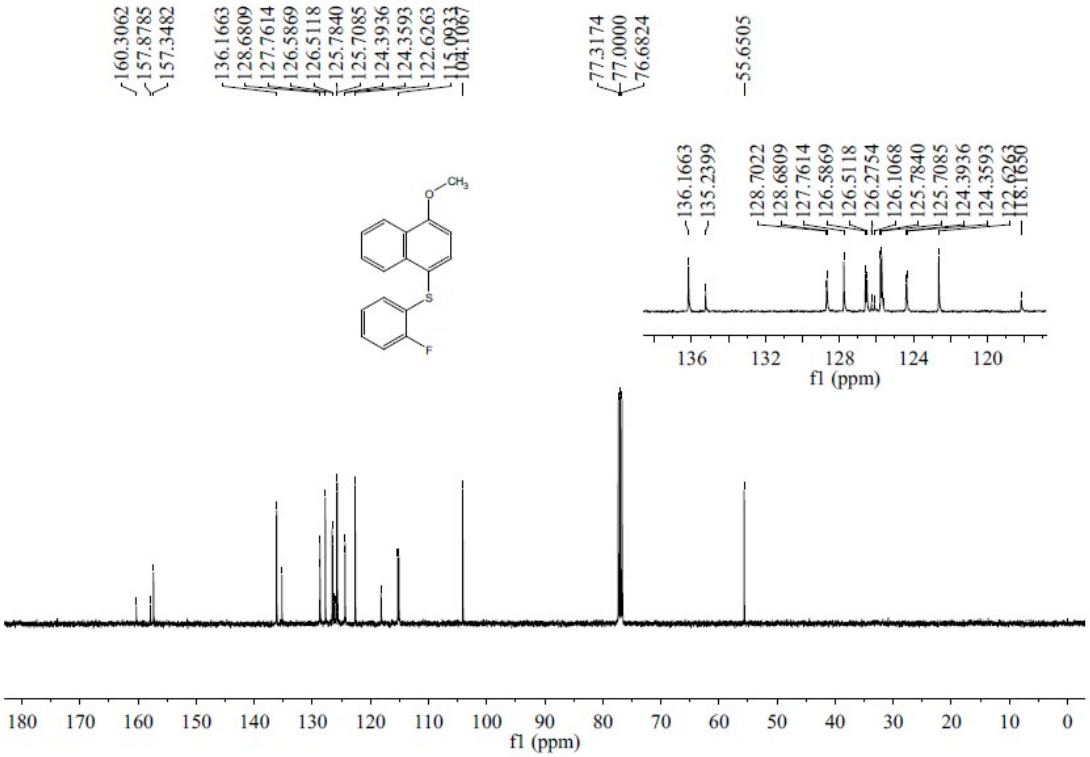


^{13}C NMR of **3an**



^{1}H NMR of **3ao**



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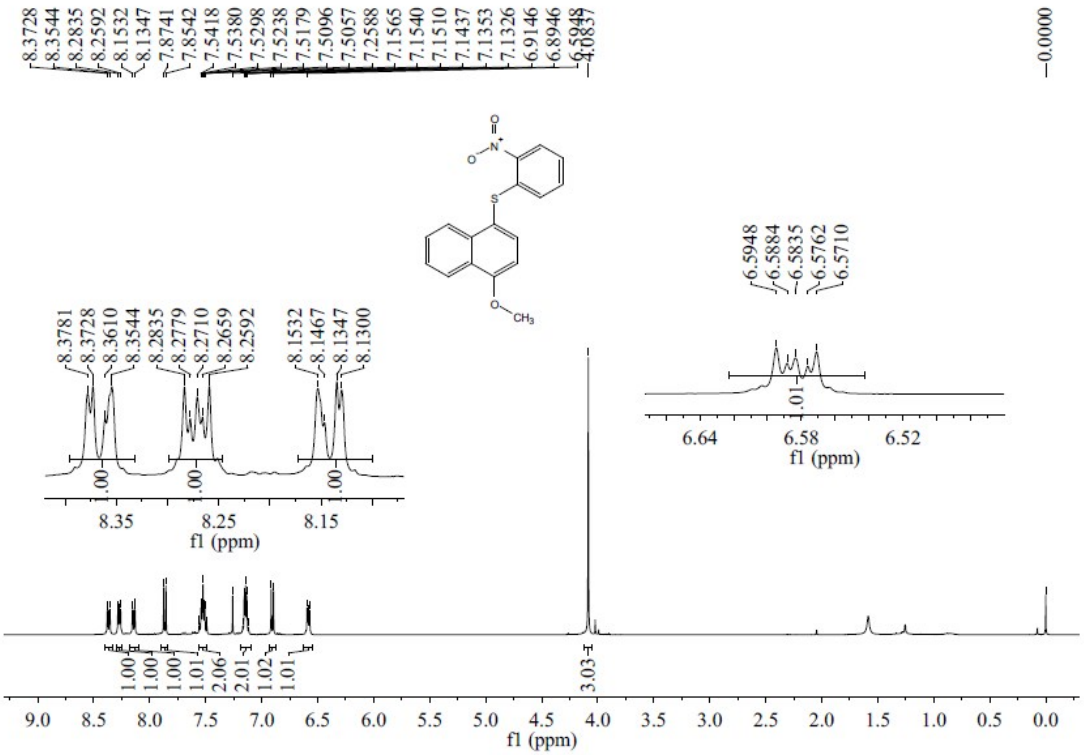
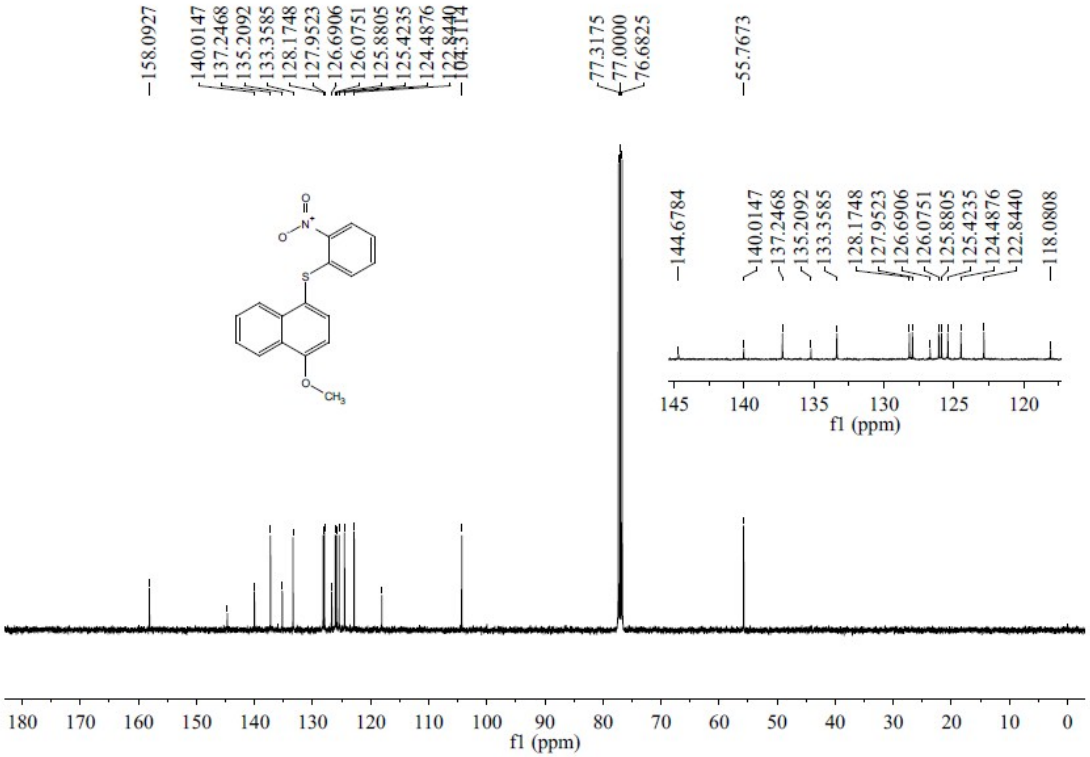
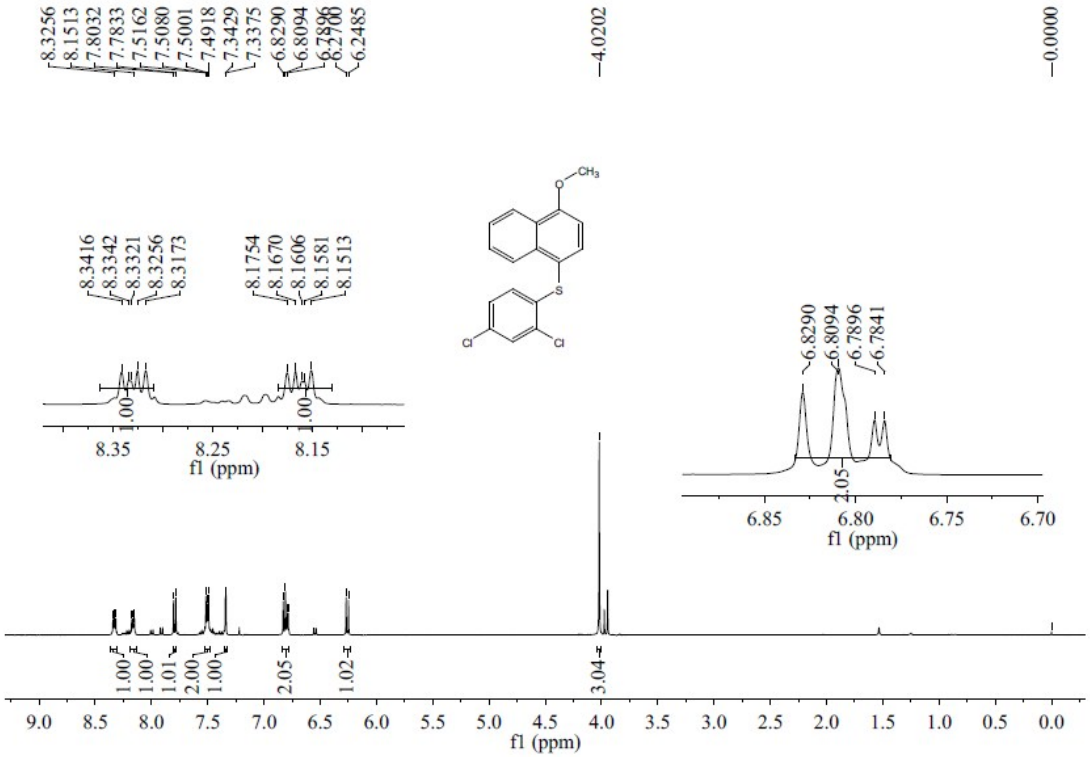


^{1}H NMR of **3ap**



^{13}C NMR of **3ap**



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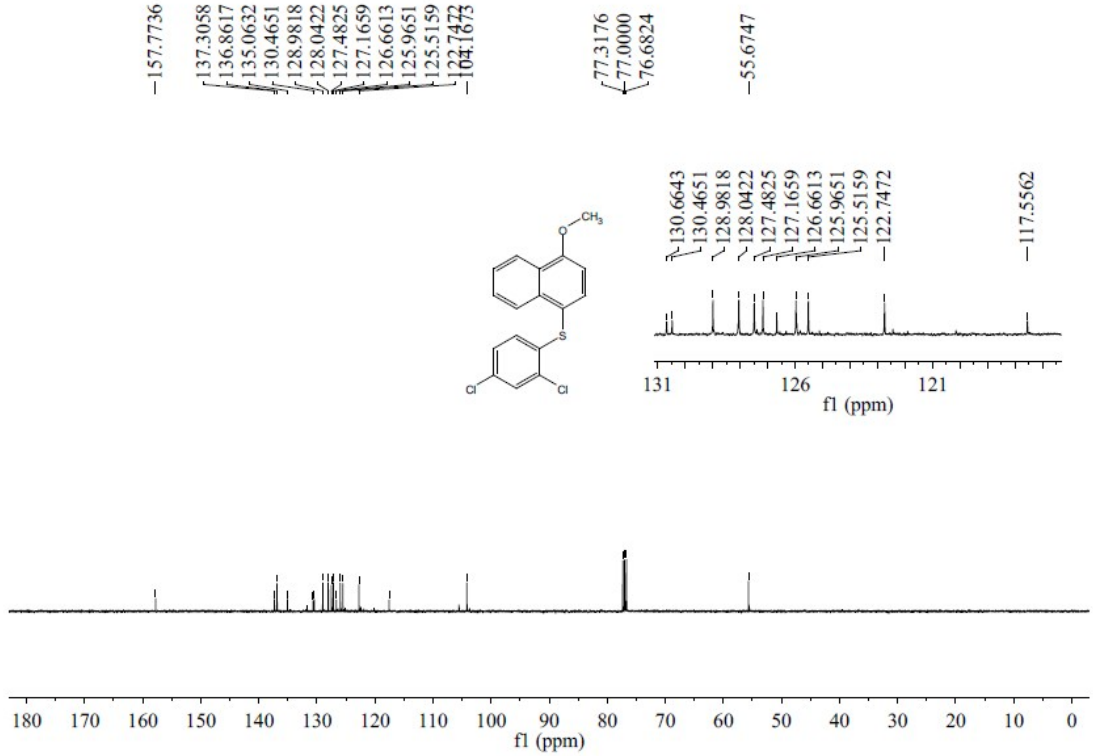

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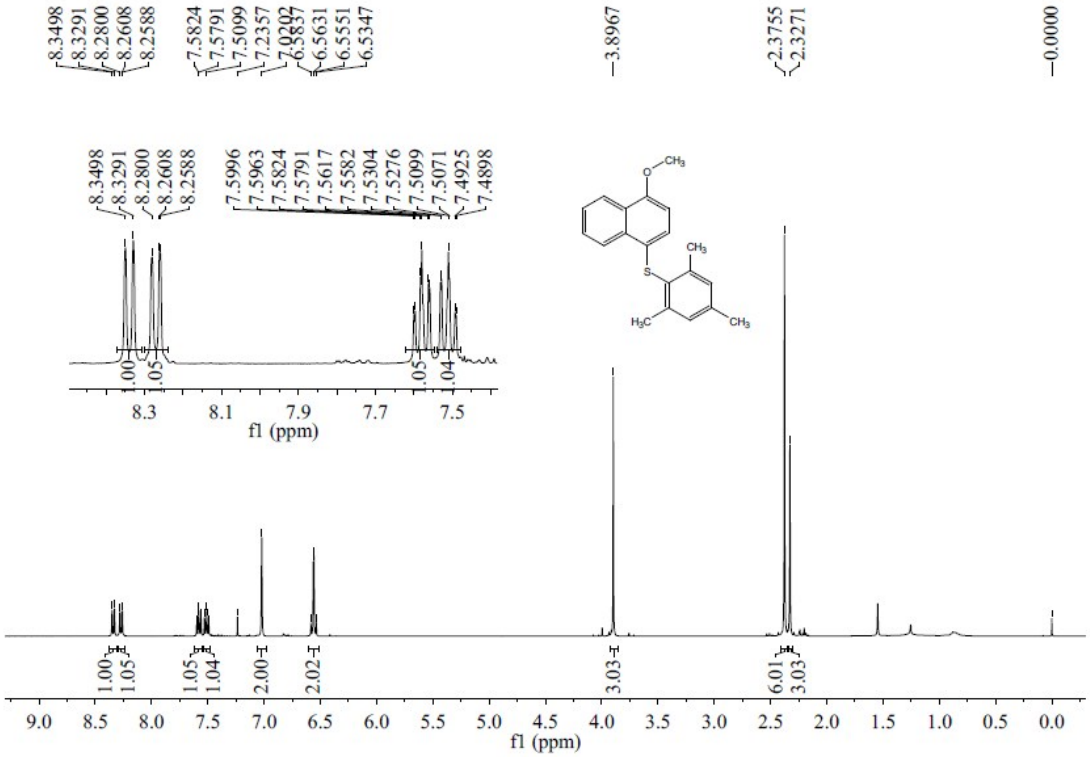

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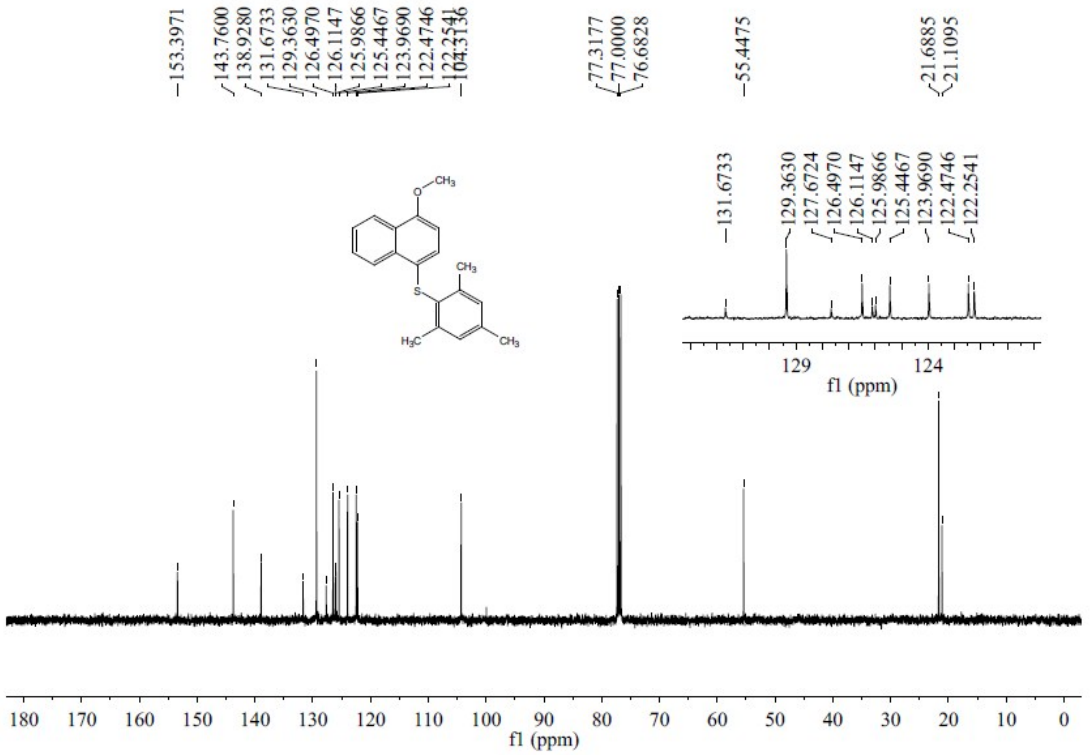
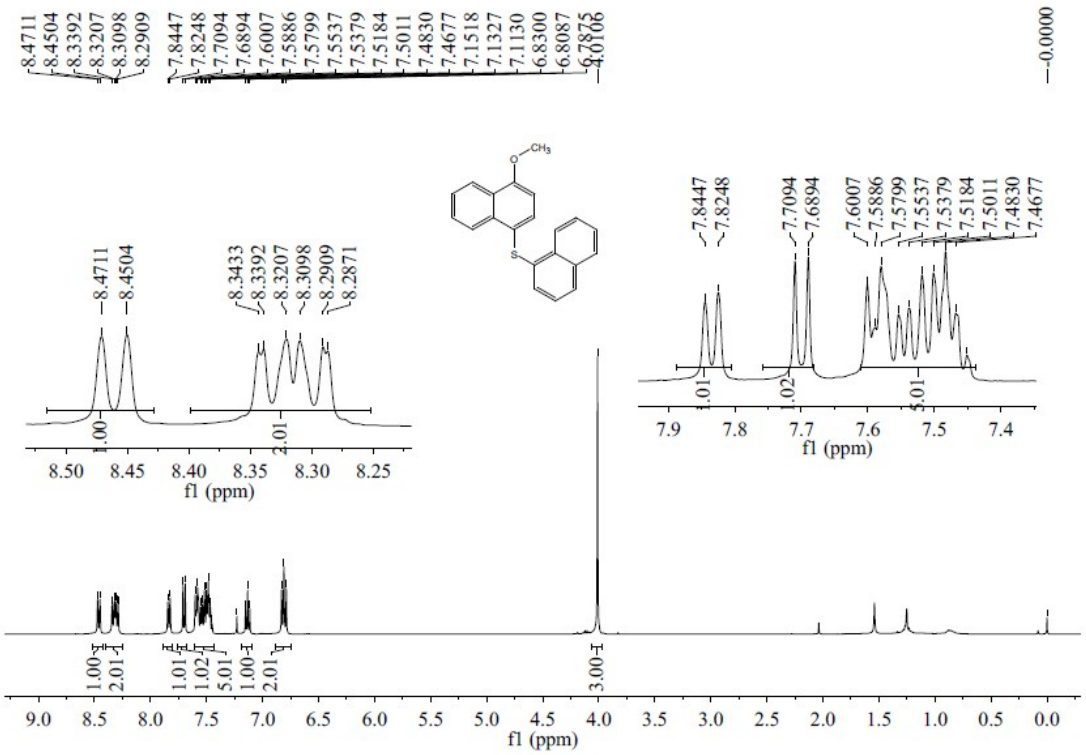
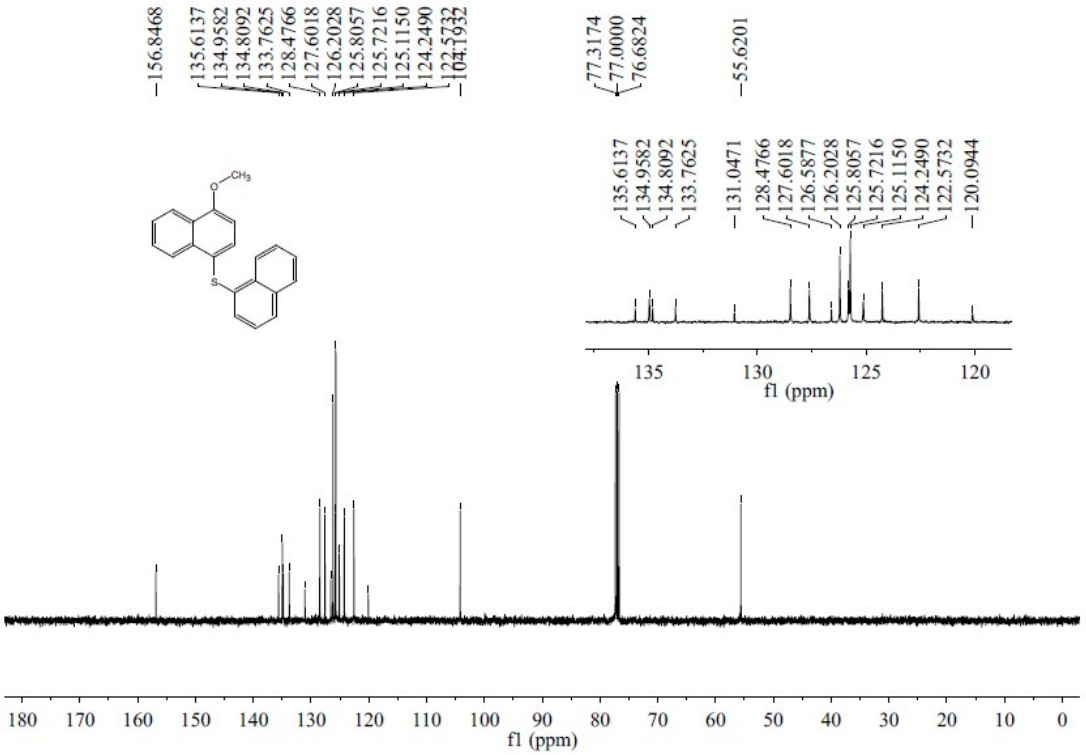


^{13}C NMR of **3ar**



^{1}H NMR of **3as**



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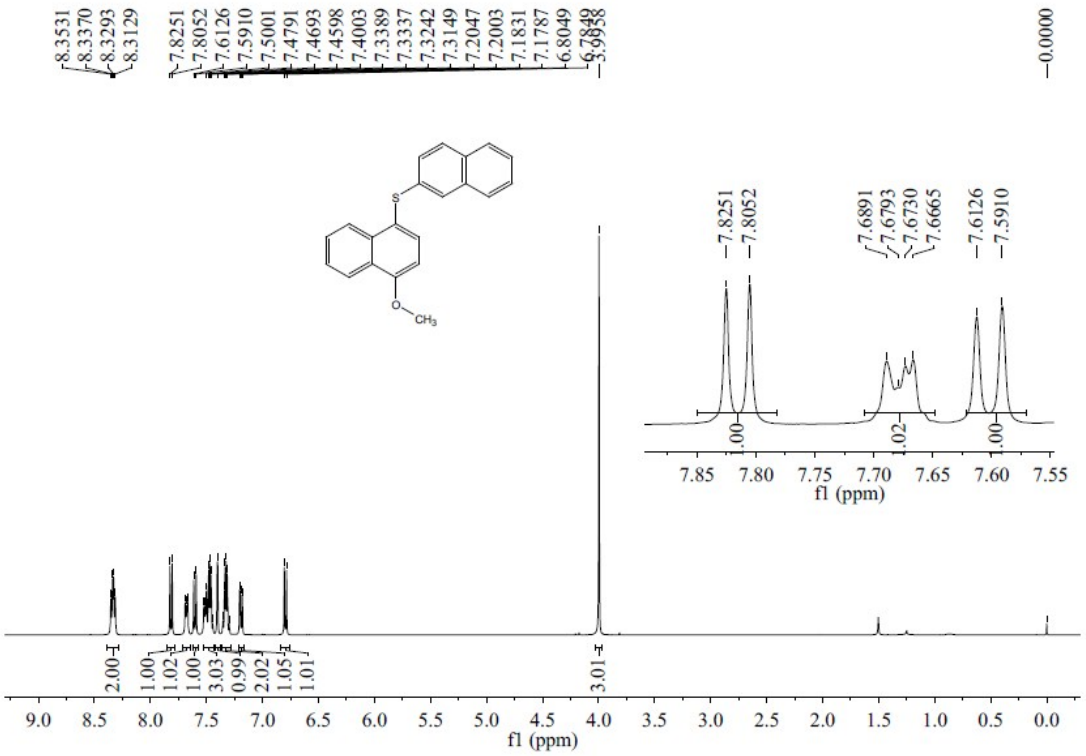
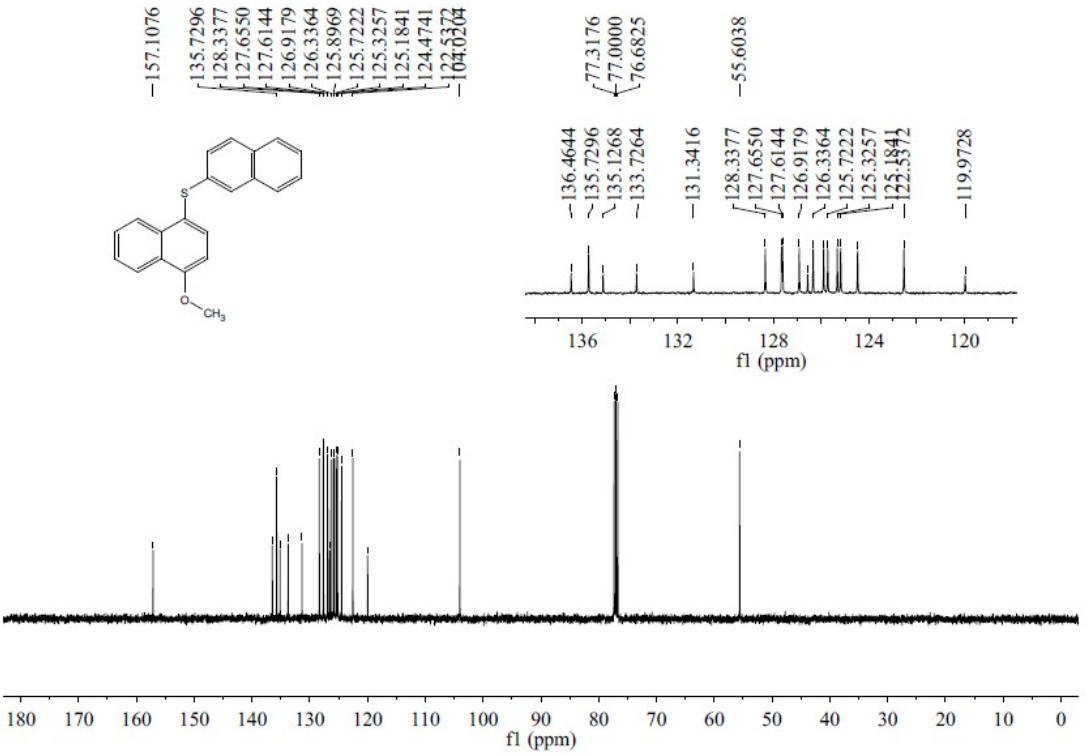
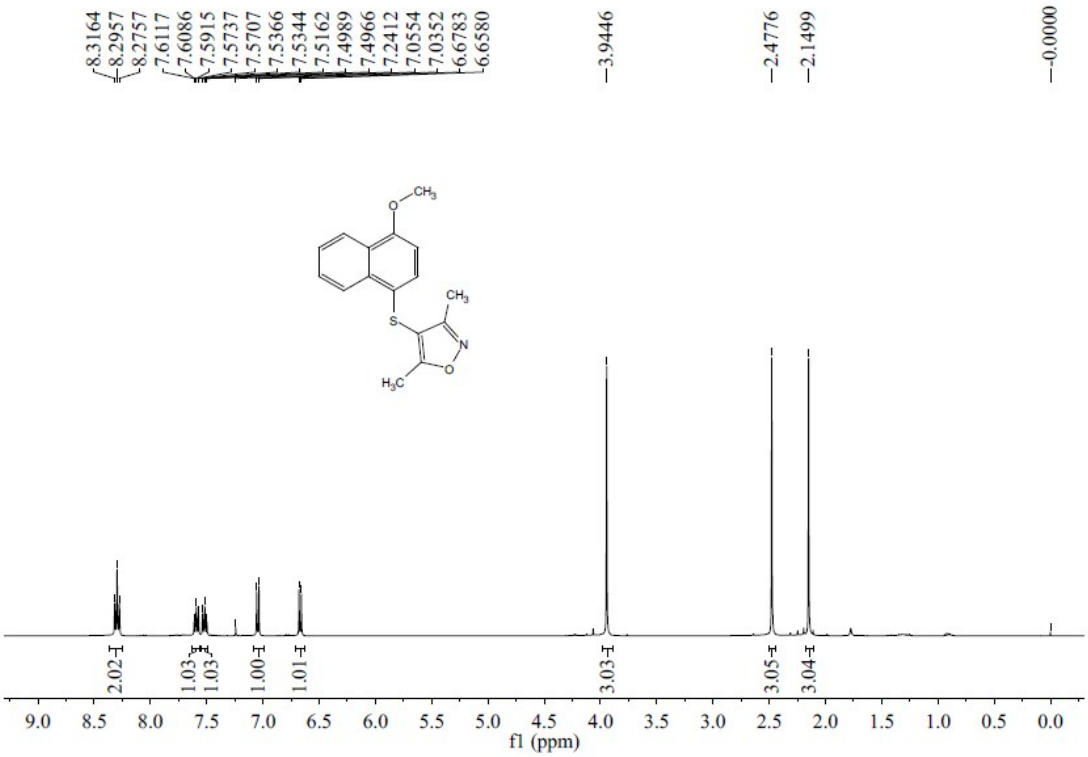


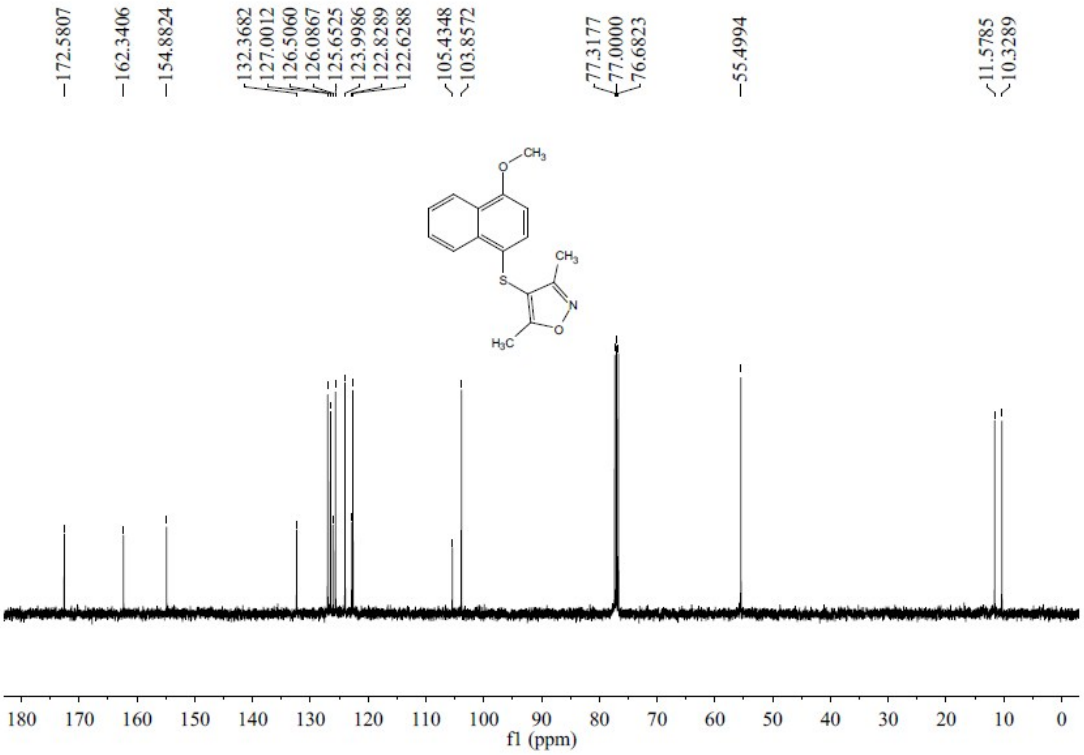
^{1}H NMR of **3at**



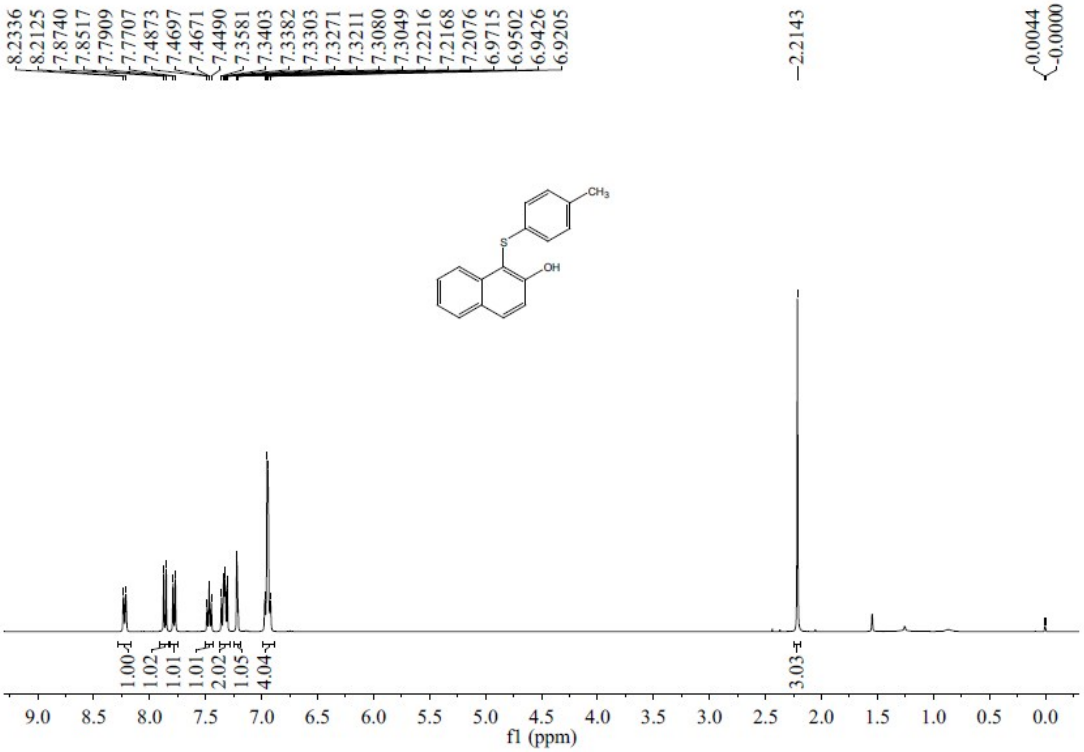
^{13}C NMR of **3at**



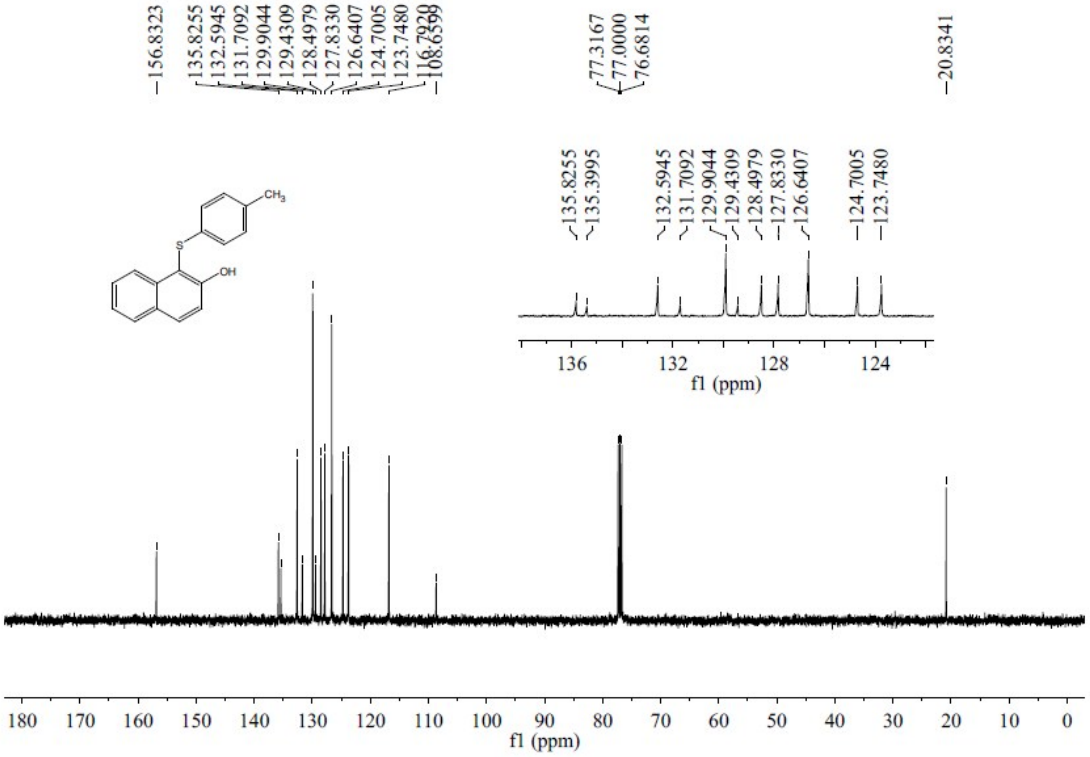
^{1}H NMR of **3au**



^{13}C NMR of **3au**



^{1}H NMR of **4aa**



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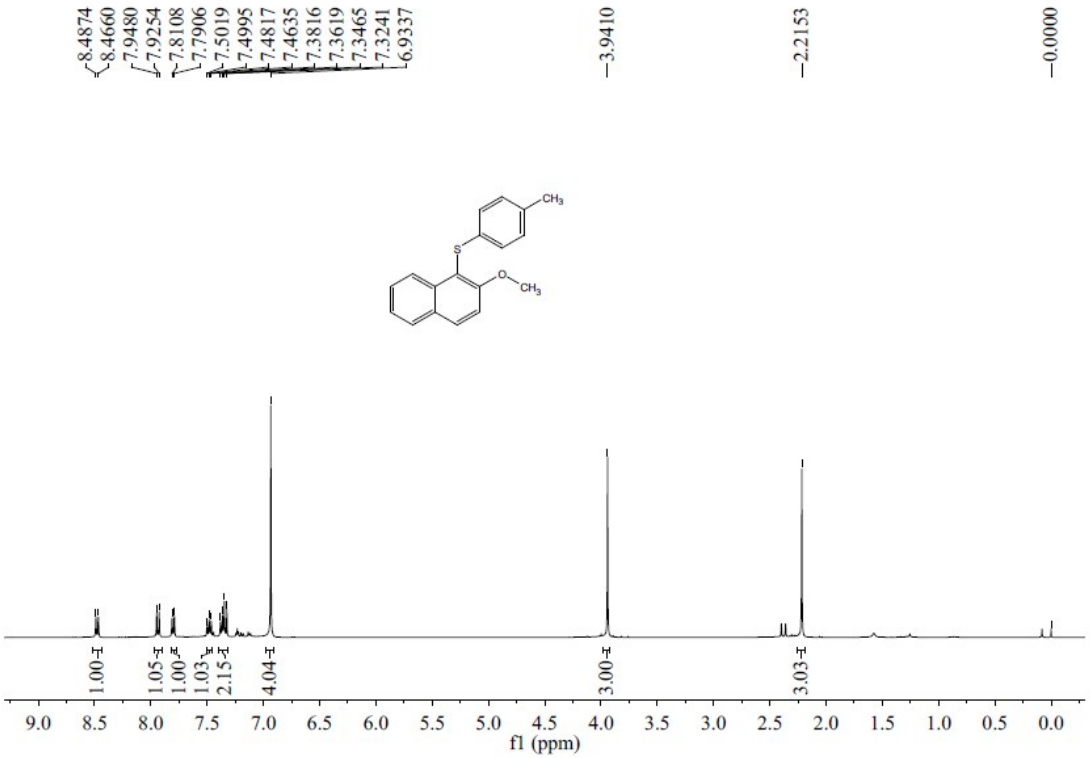

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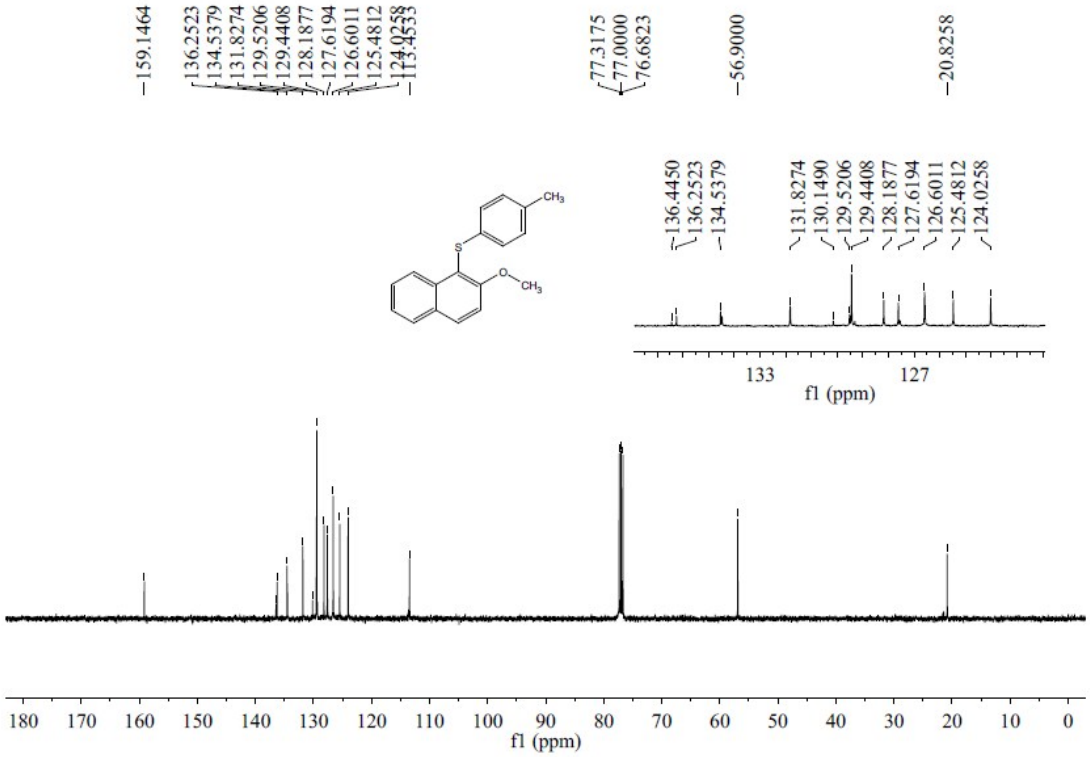
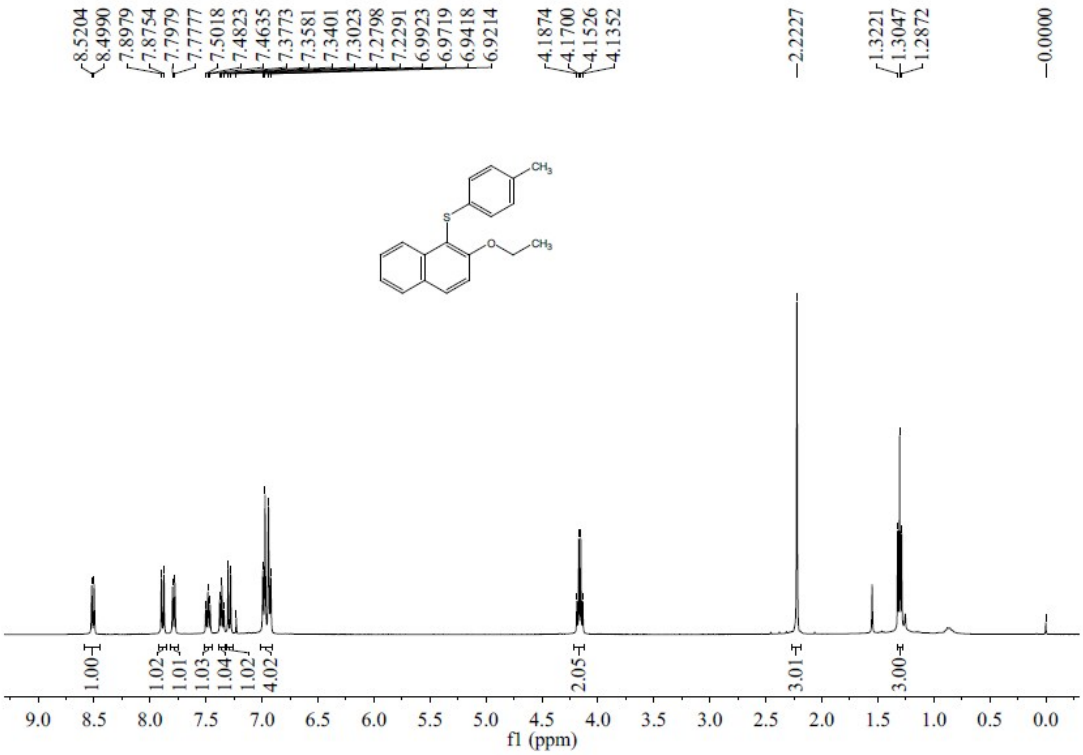
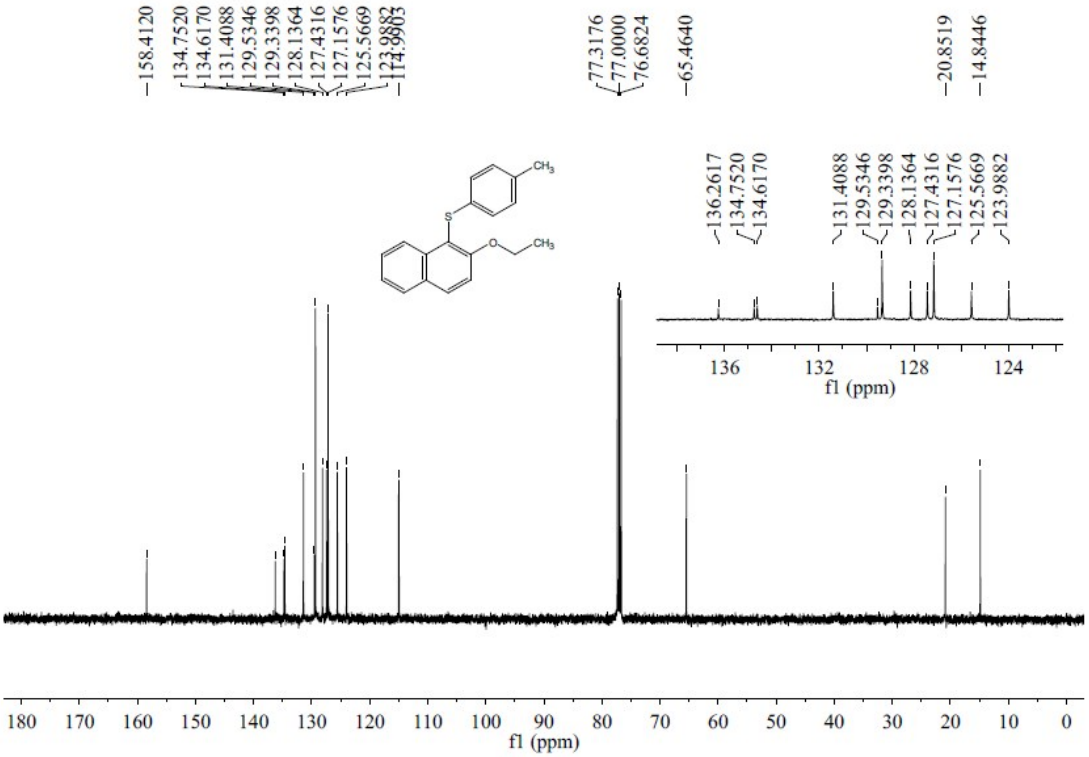


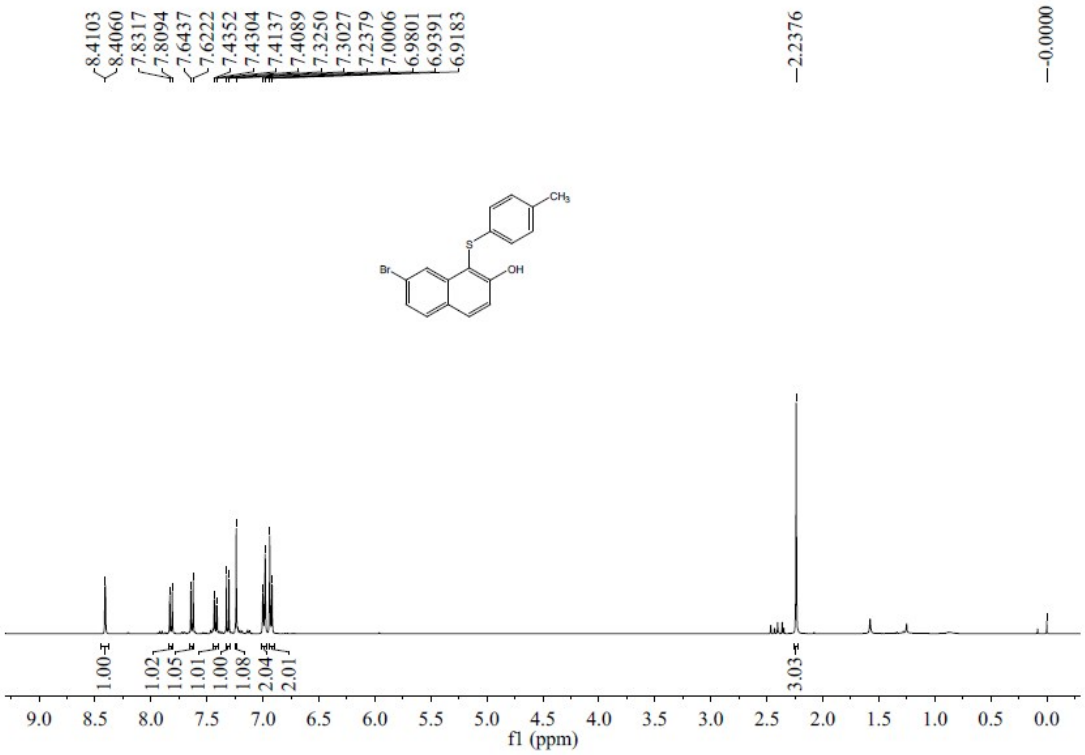
^{13}C NMR of **4ab**



^{1}H NMR of **4ac**



^{13}C NMR of **4ac**



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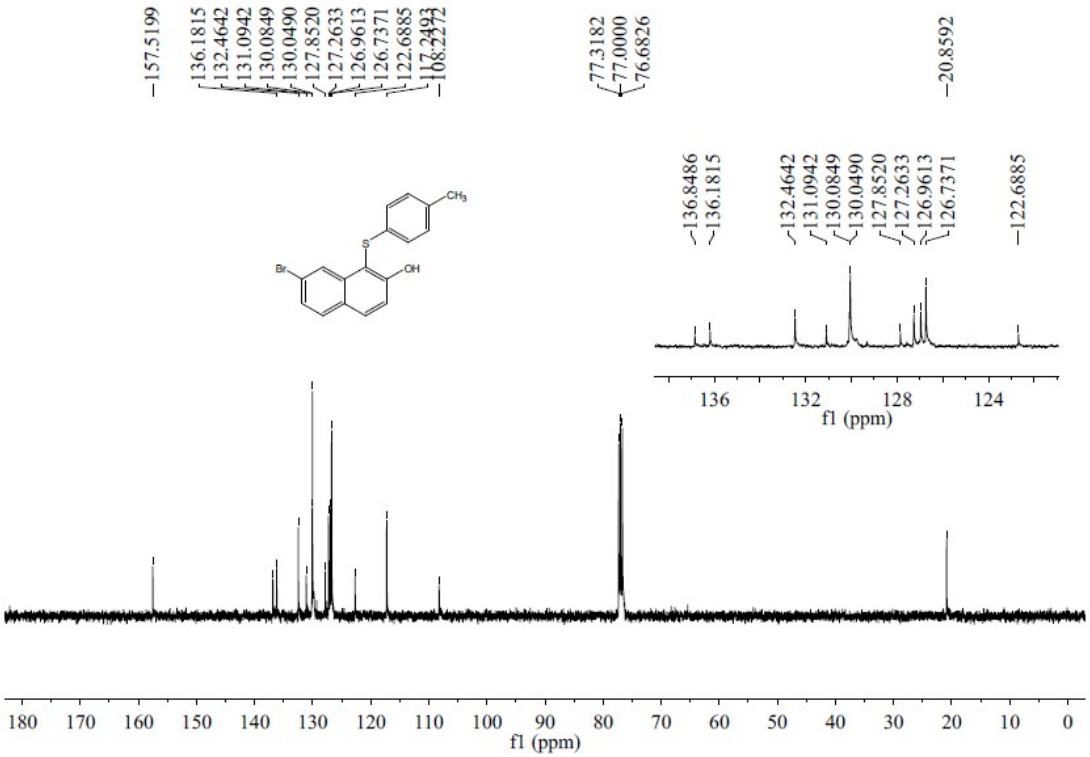
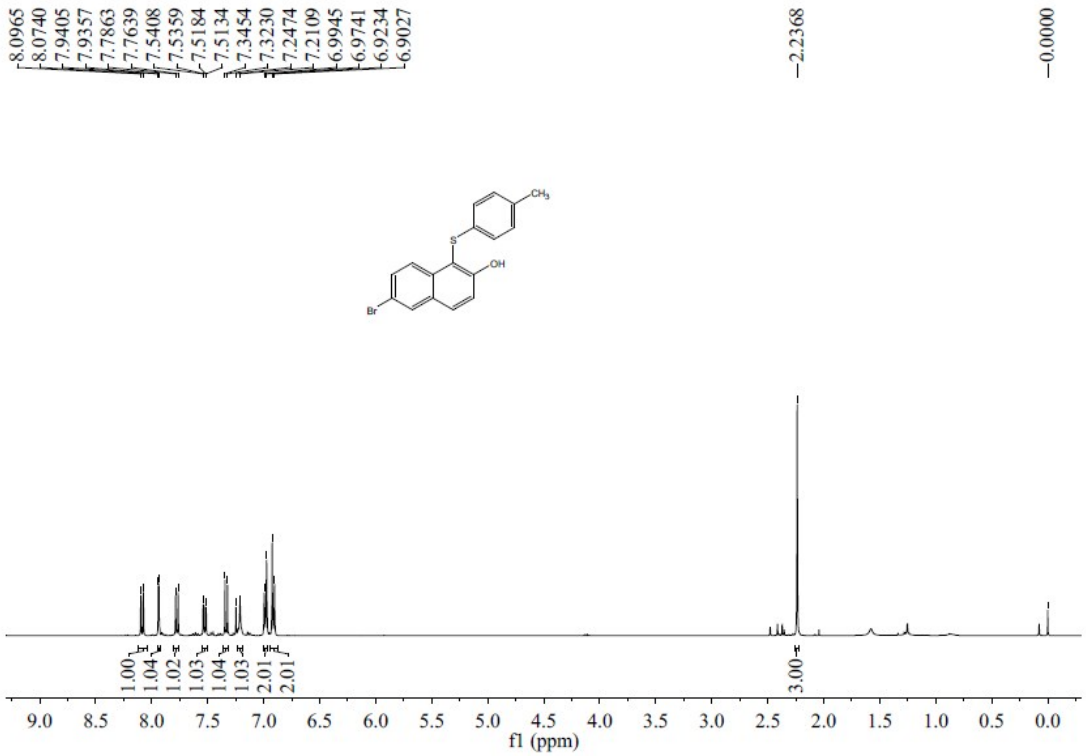
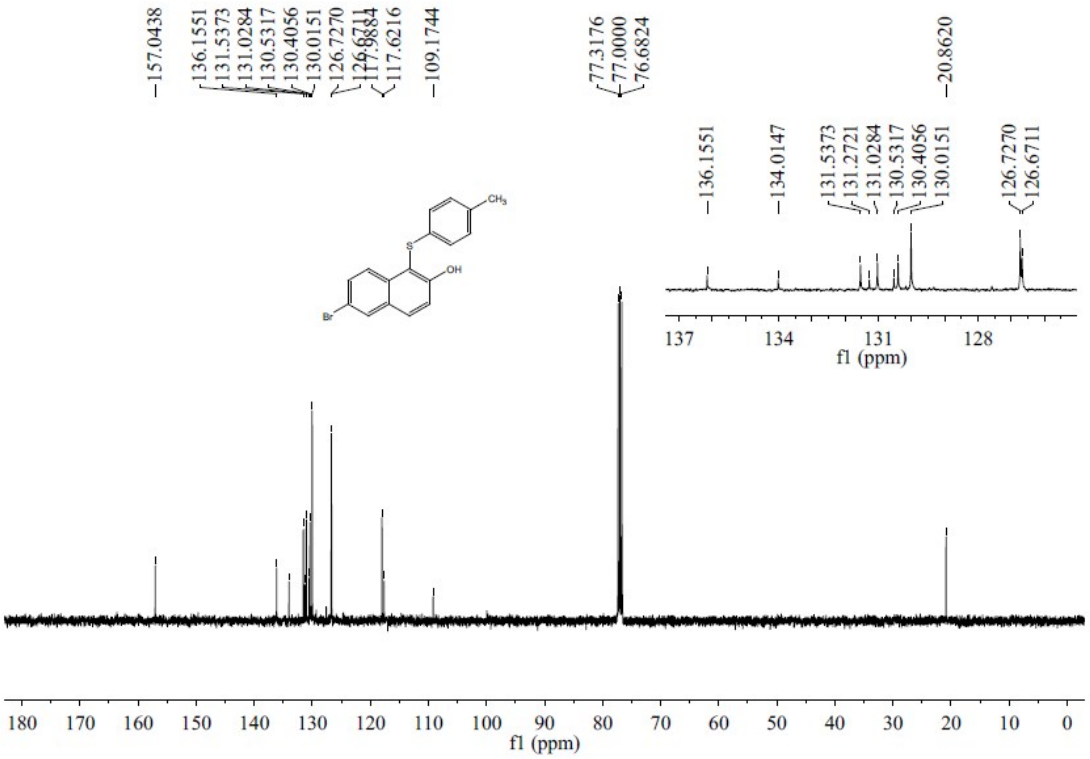


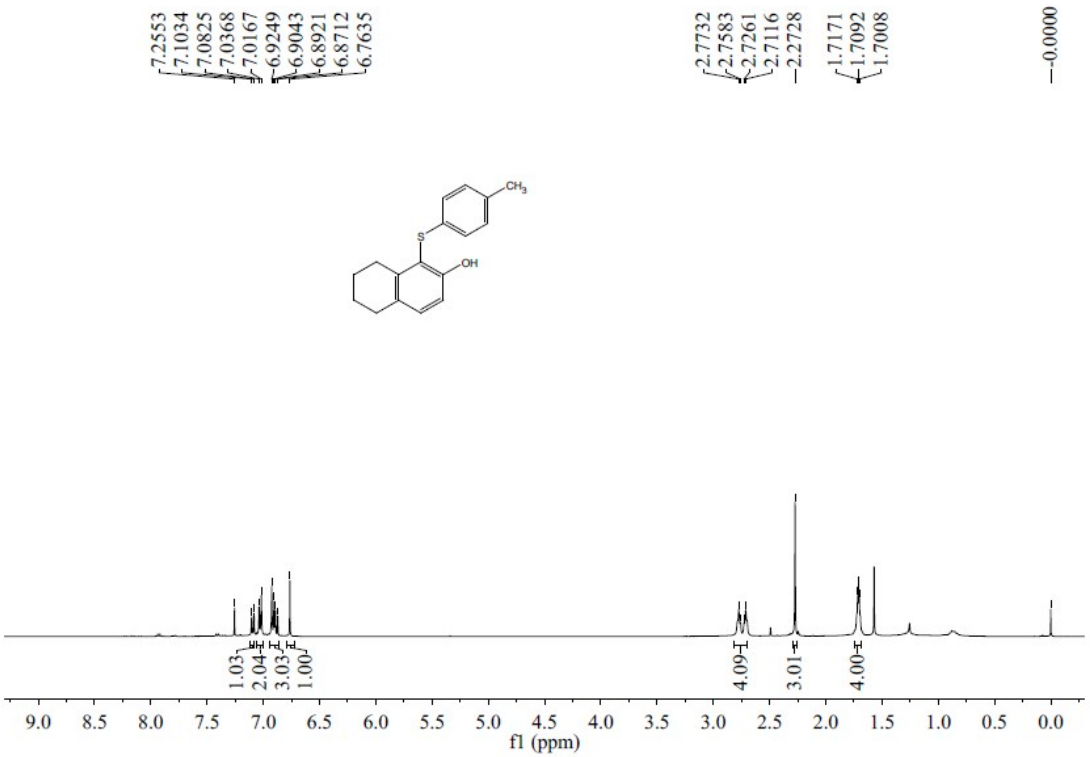
^{13}C NMR of **4ad**



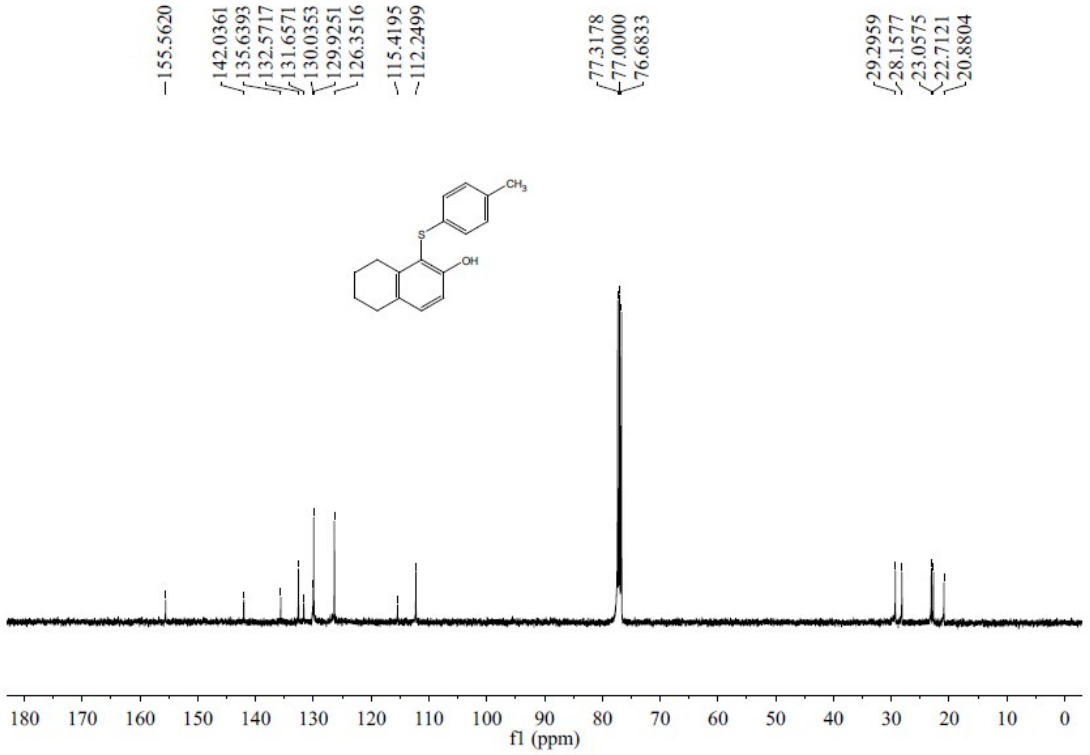
^{1}H NMR of **4ae**



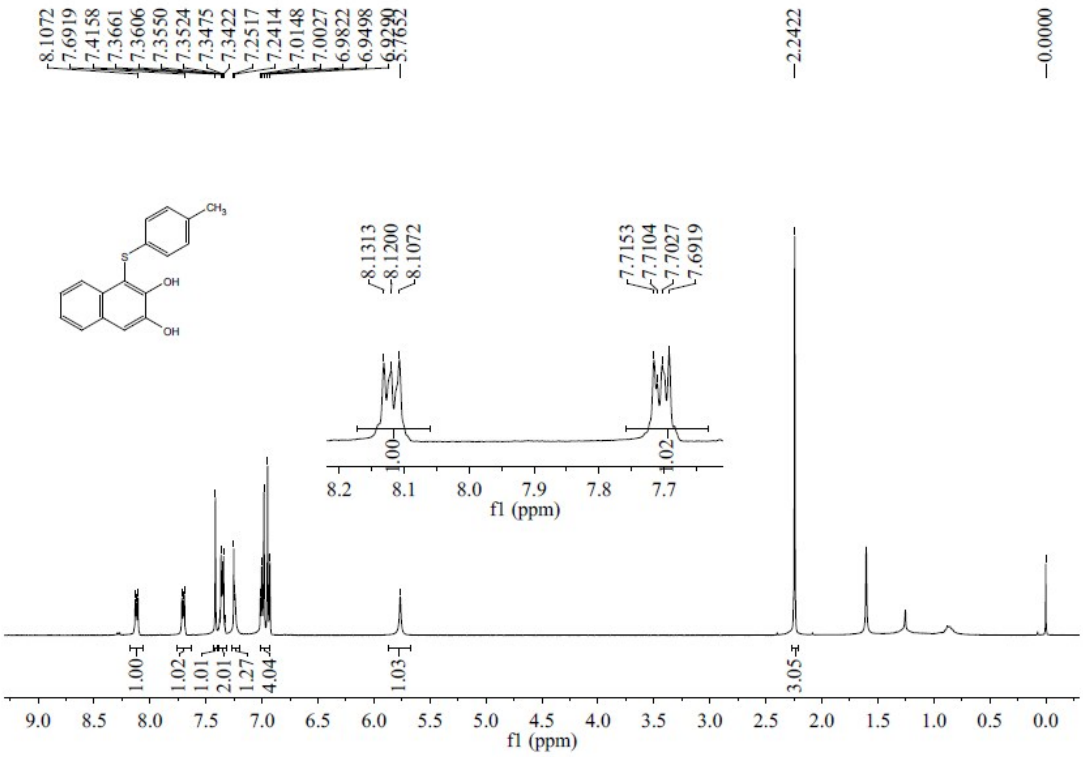
^{13}C NMR of **4ae**



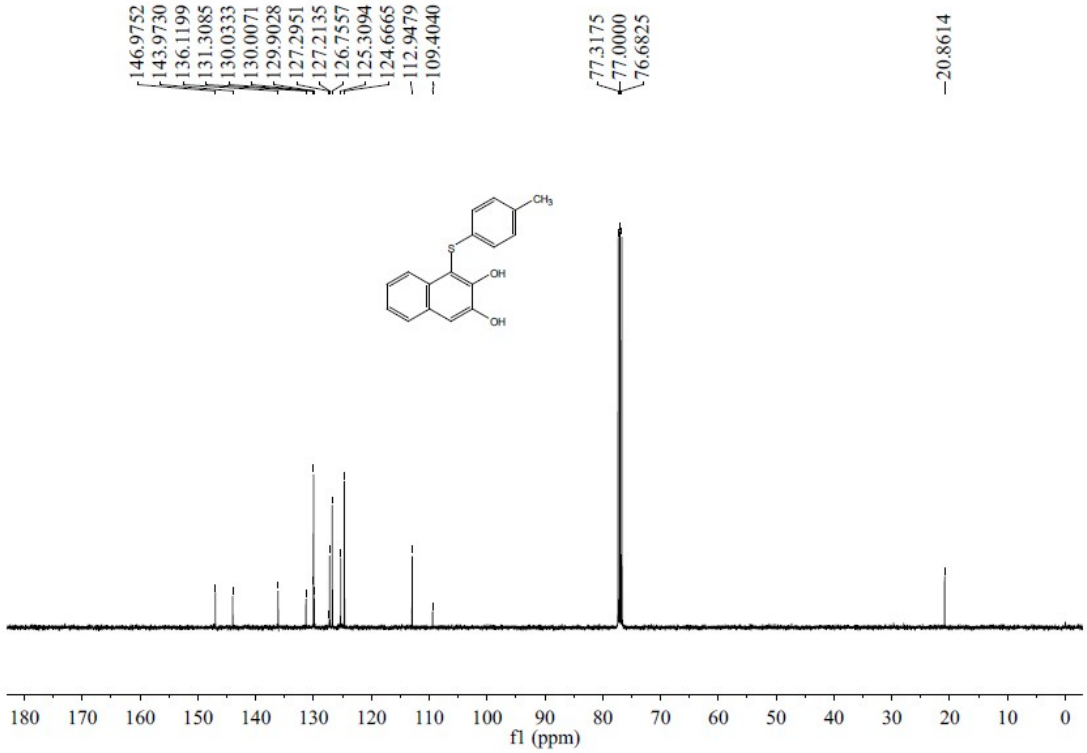
^{1}H NMR of **4af**



^{13}C NMR of **4af**



^{1}H NMR of **4ag**



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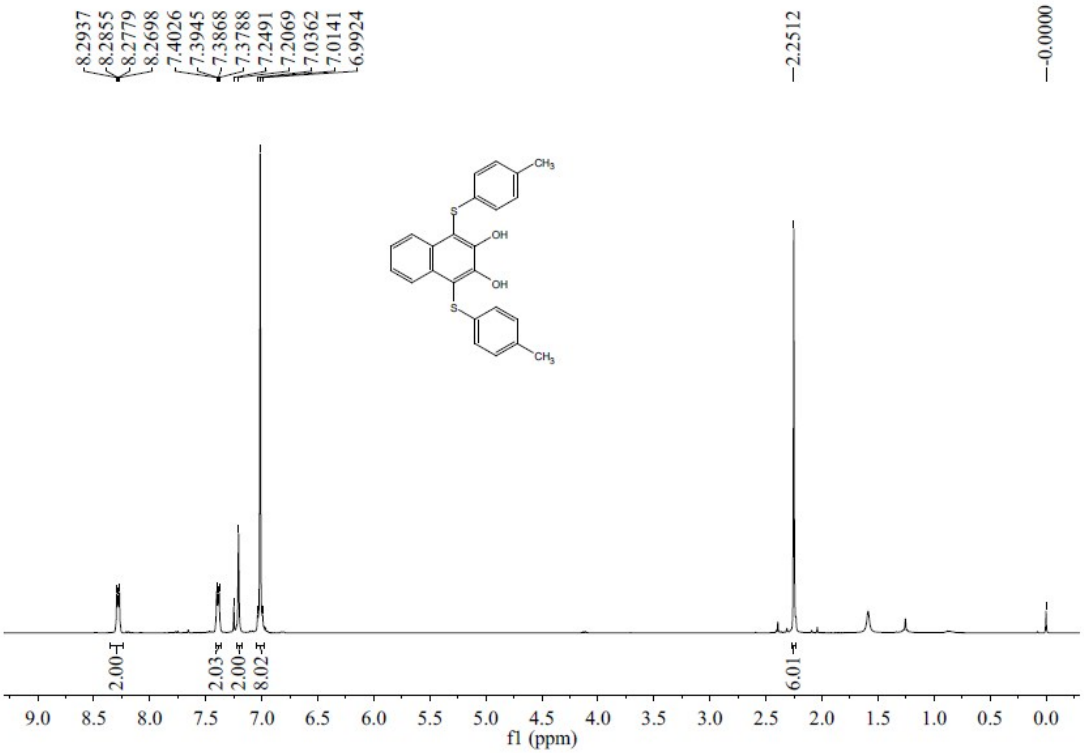
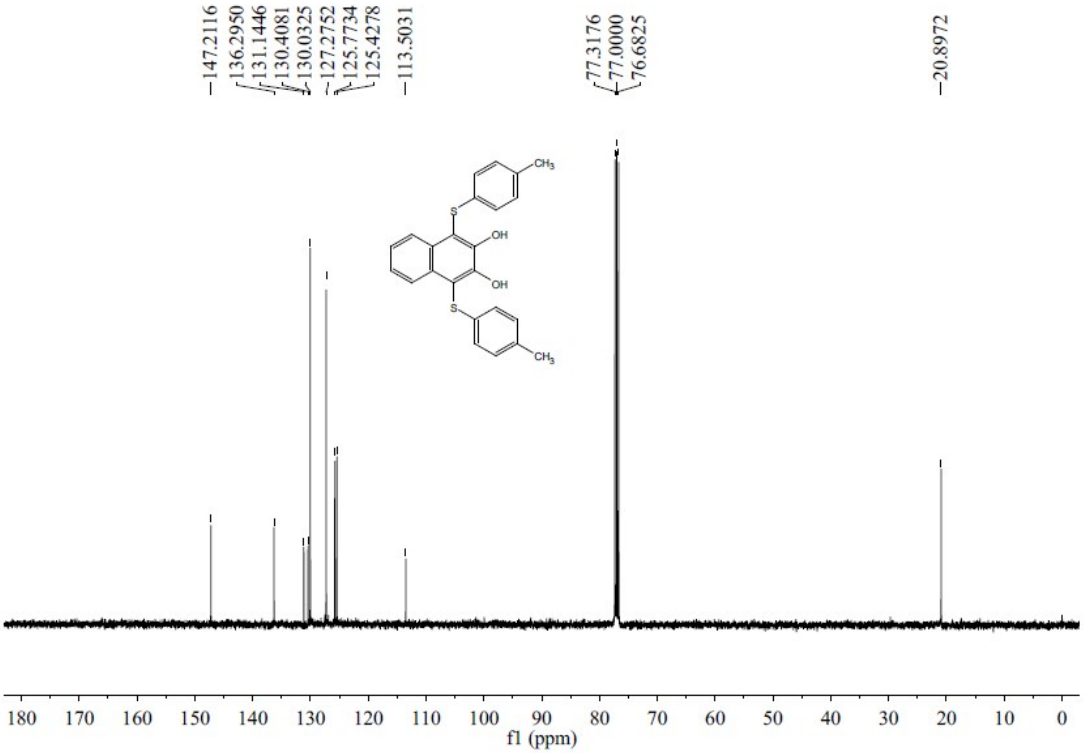
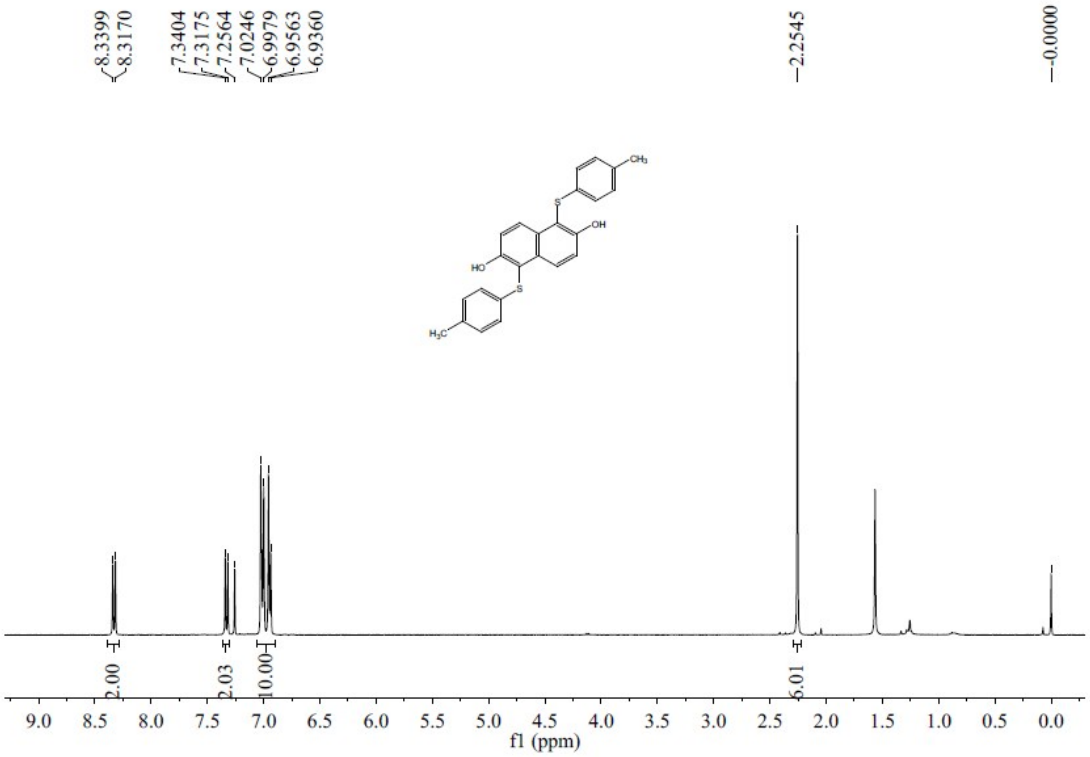


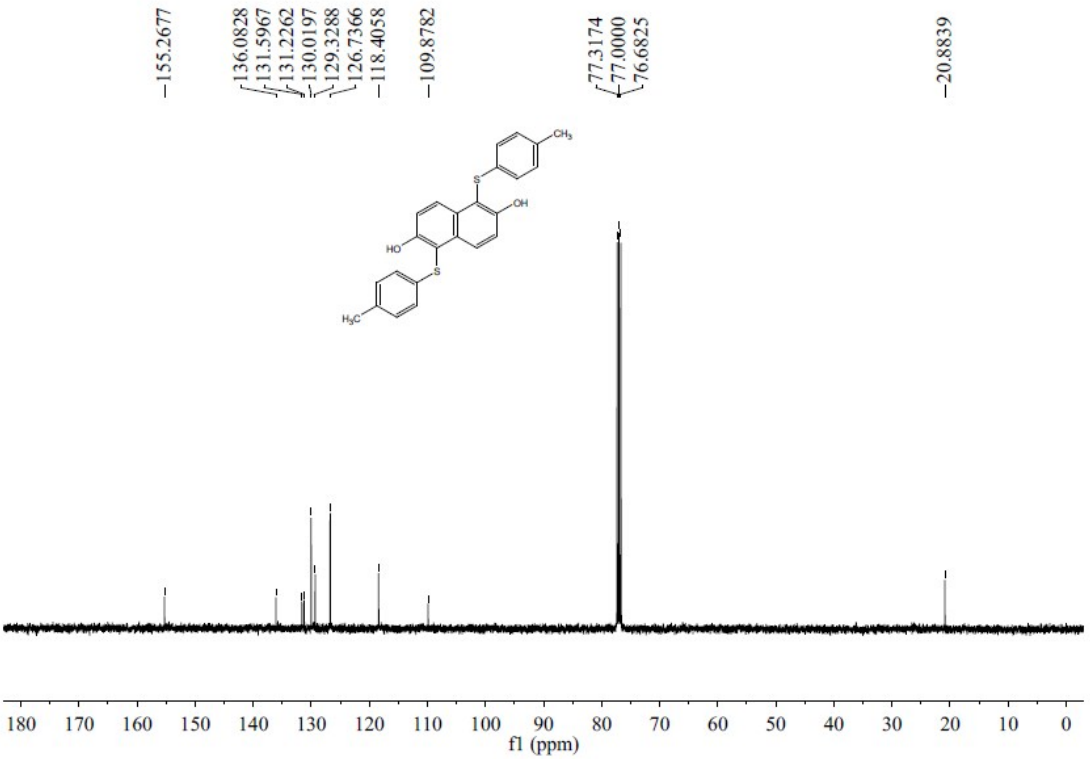
^{1}H NMR of **4ah**



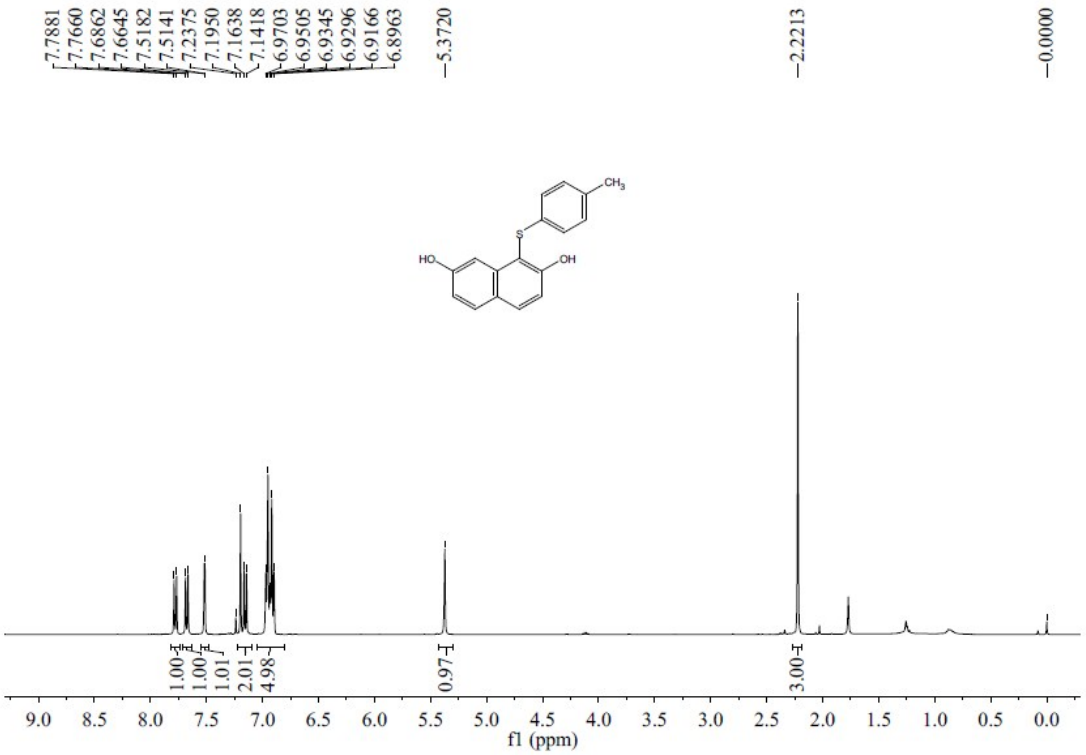
^{13}C NMR of **4ah**



^{1}H NMR of **4ai**



^{13}C NMR of **4ai**



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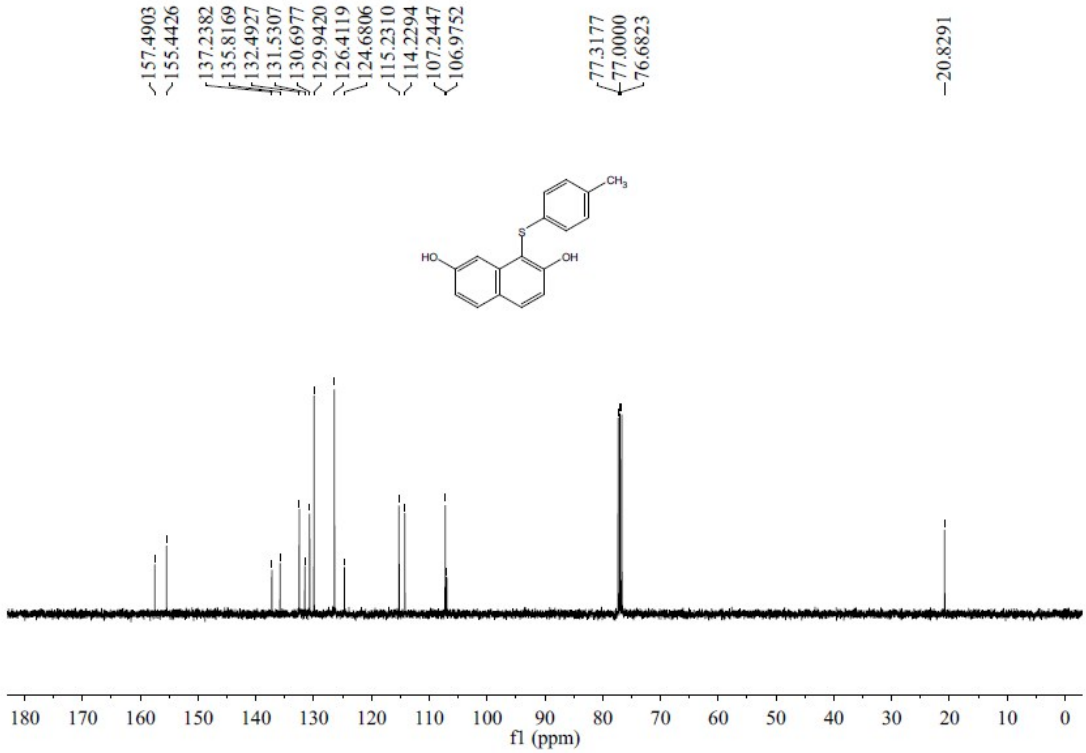
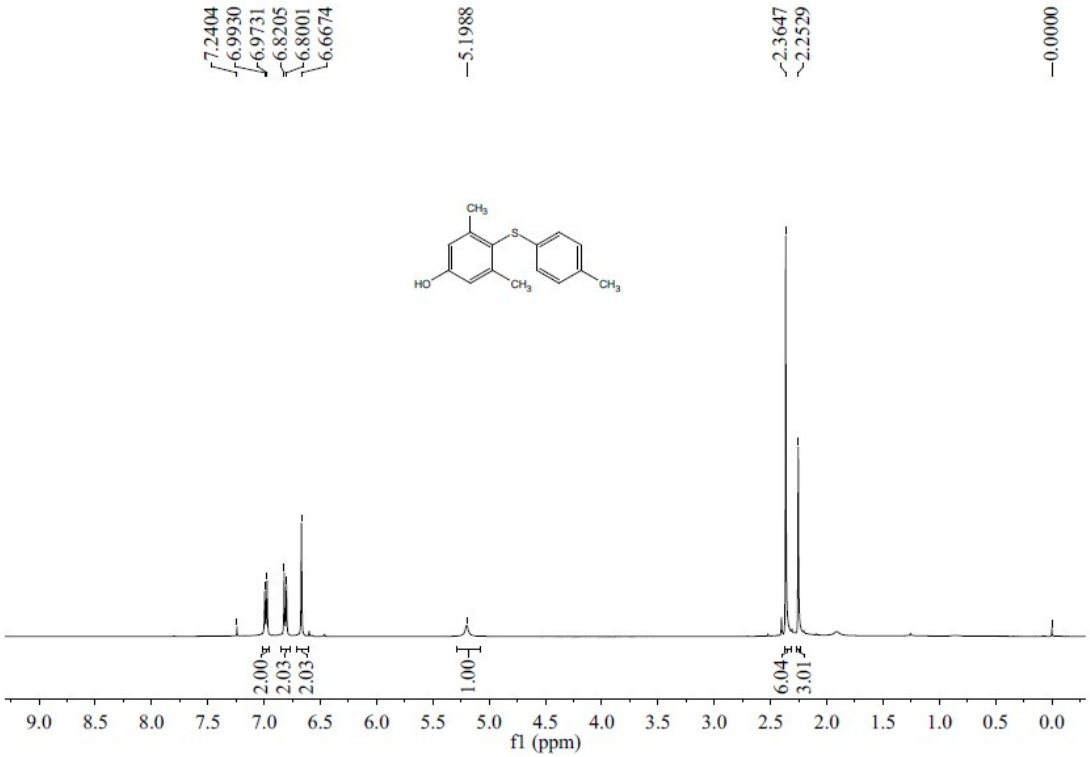
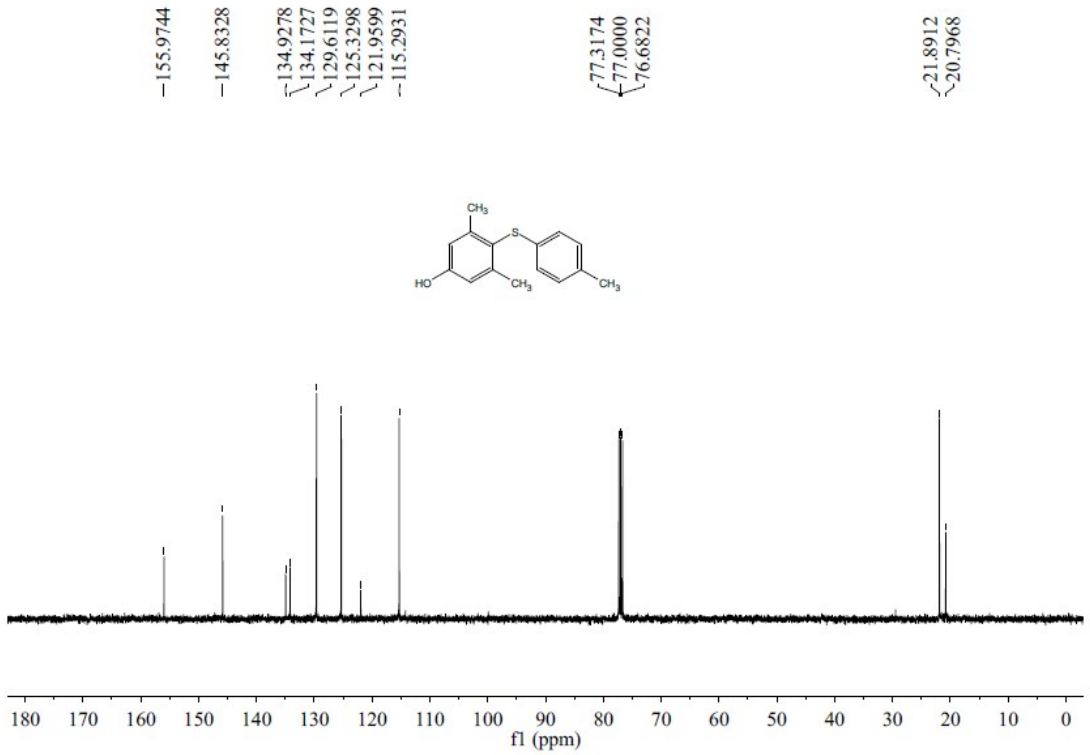


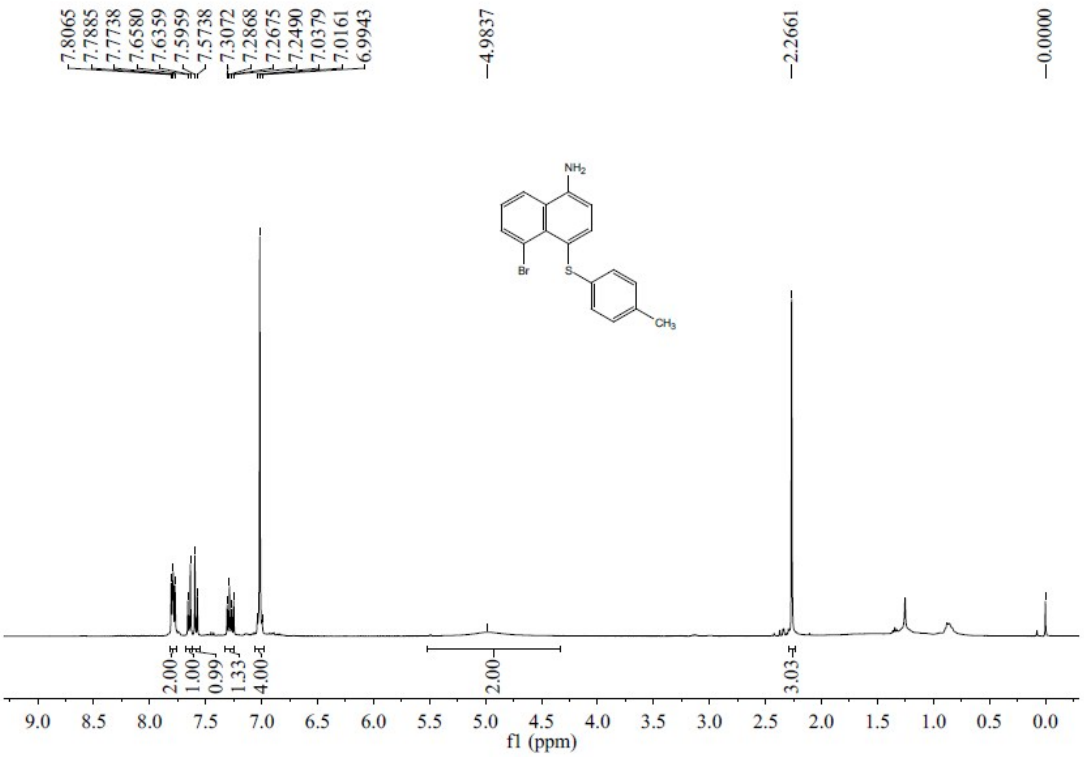
^{13}C NMR of **4aj**



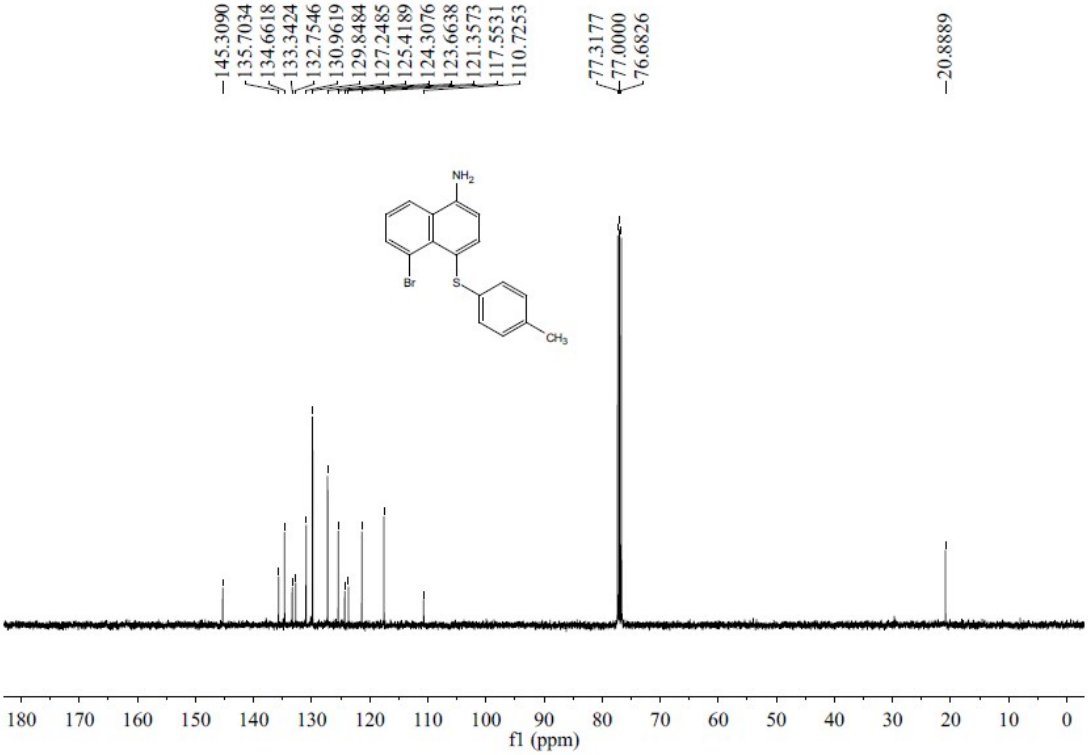
^{1}H NMR of **4ak**



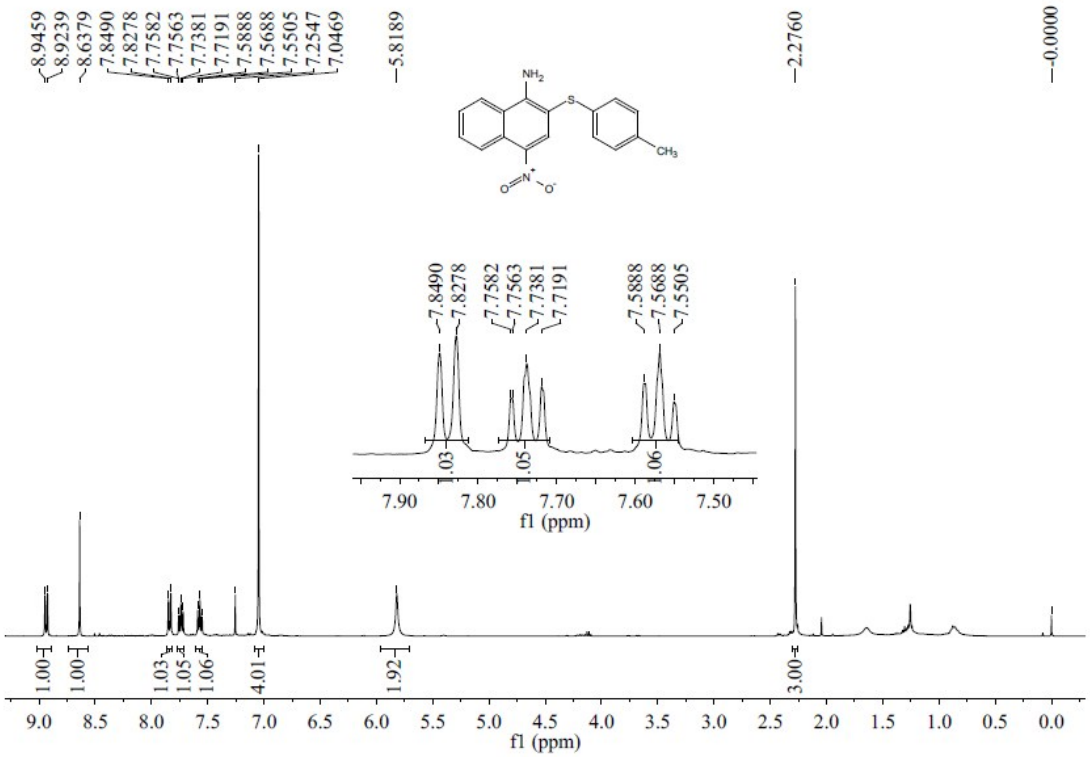
^{13}C NMR of **4ak**



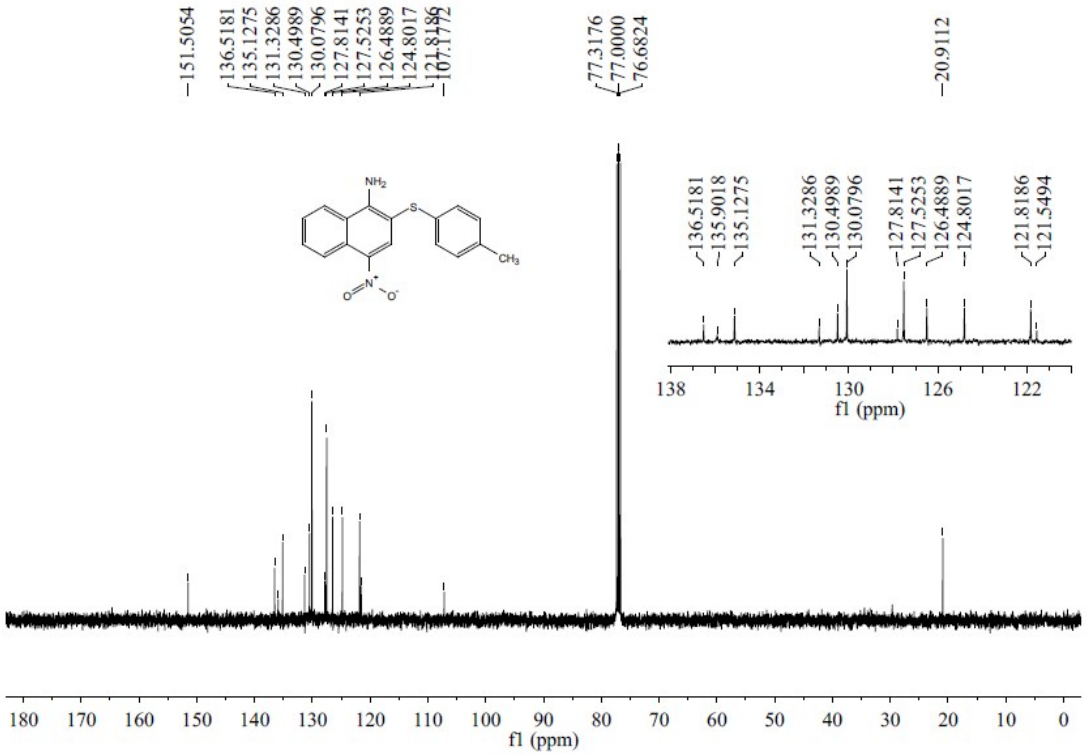
^{1}H NMR of **6aa**



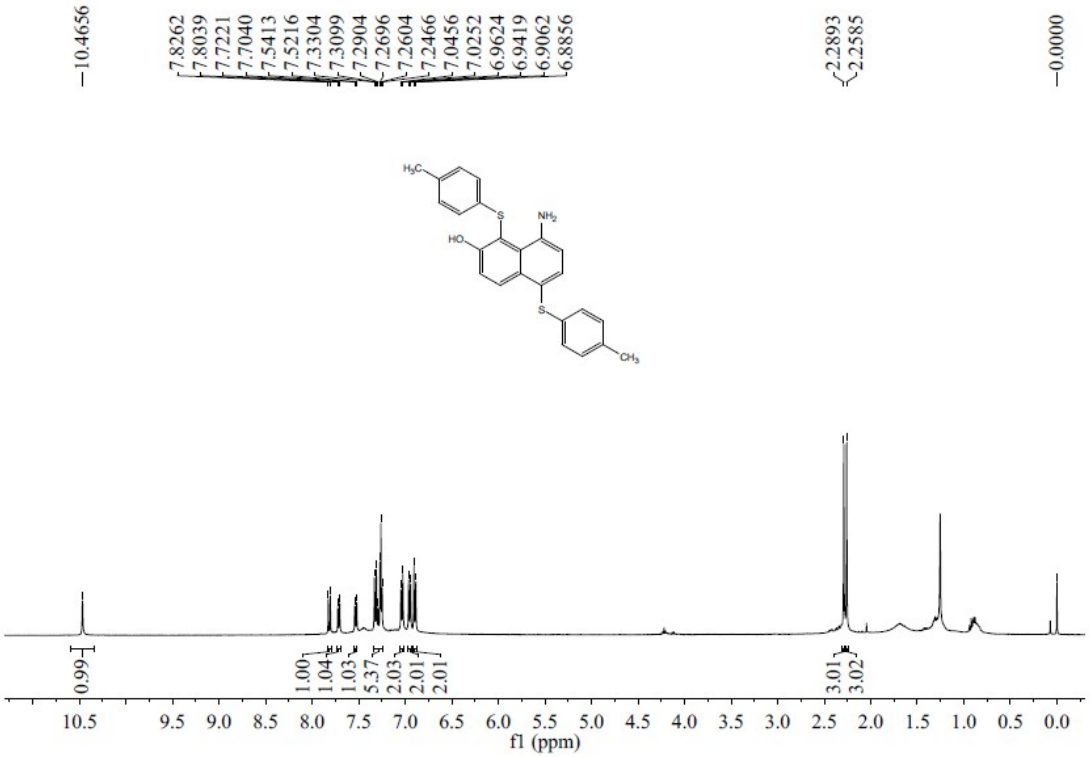
^{13}C NMR of **6aa**



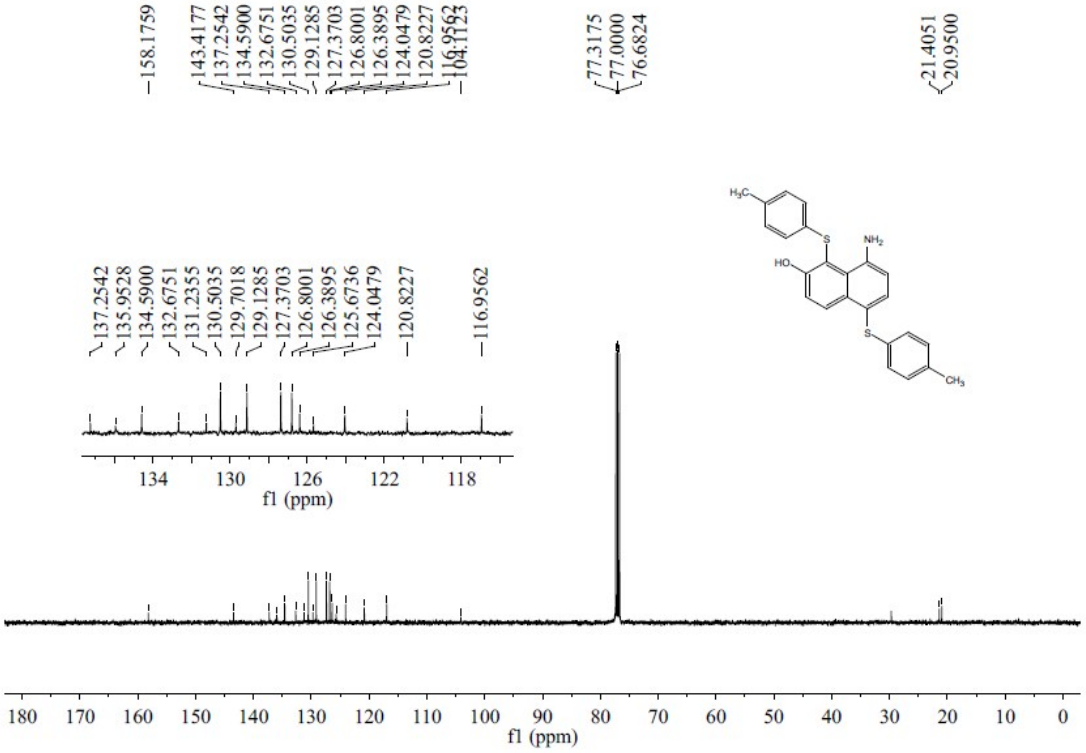
^{1}H NMR of **6ab**



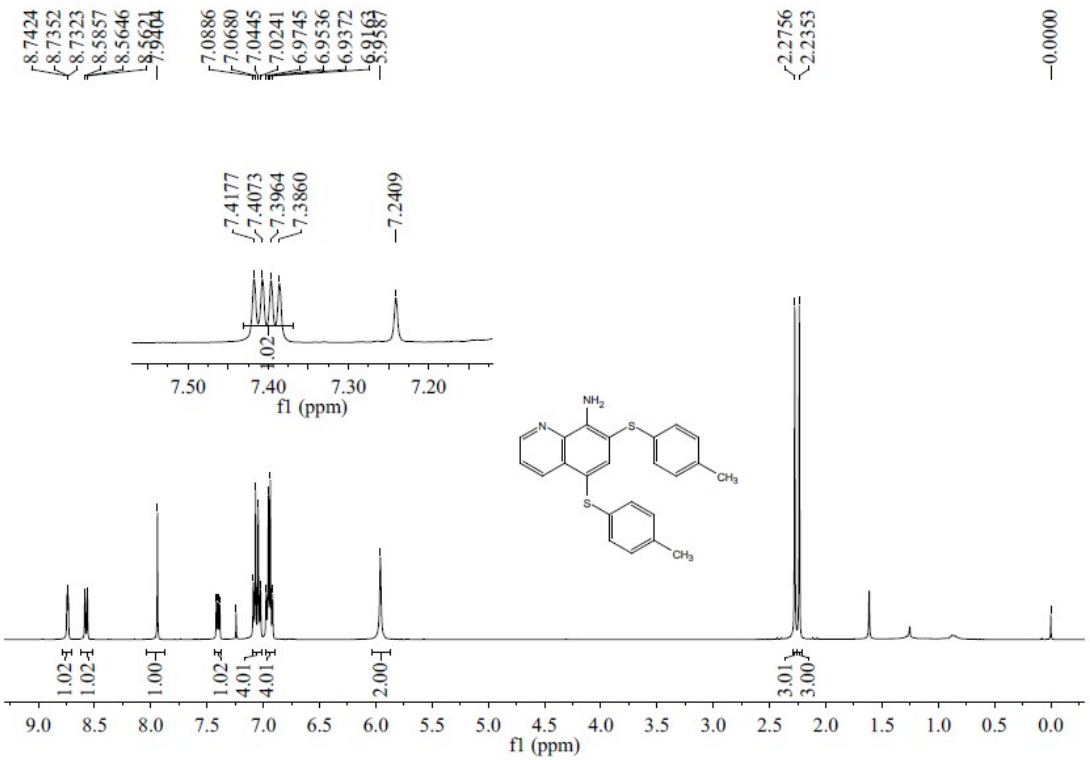
^{13}C NMR of **6ab**



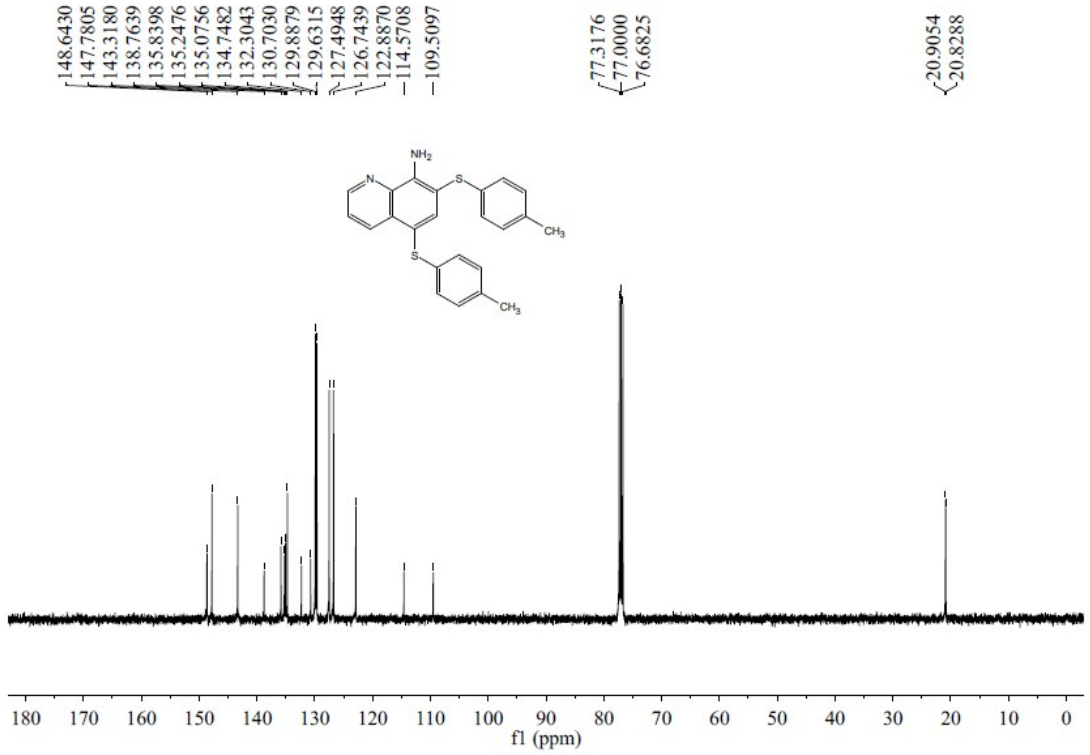
^{1}H NMR of **6ac**



^{13}C NMR of **6ac**



^{1}H NMR of **6ad**



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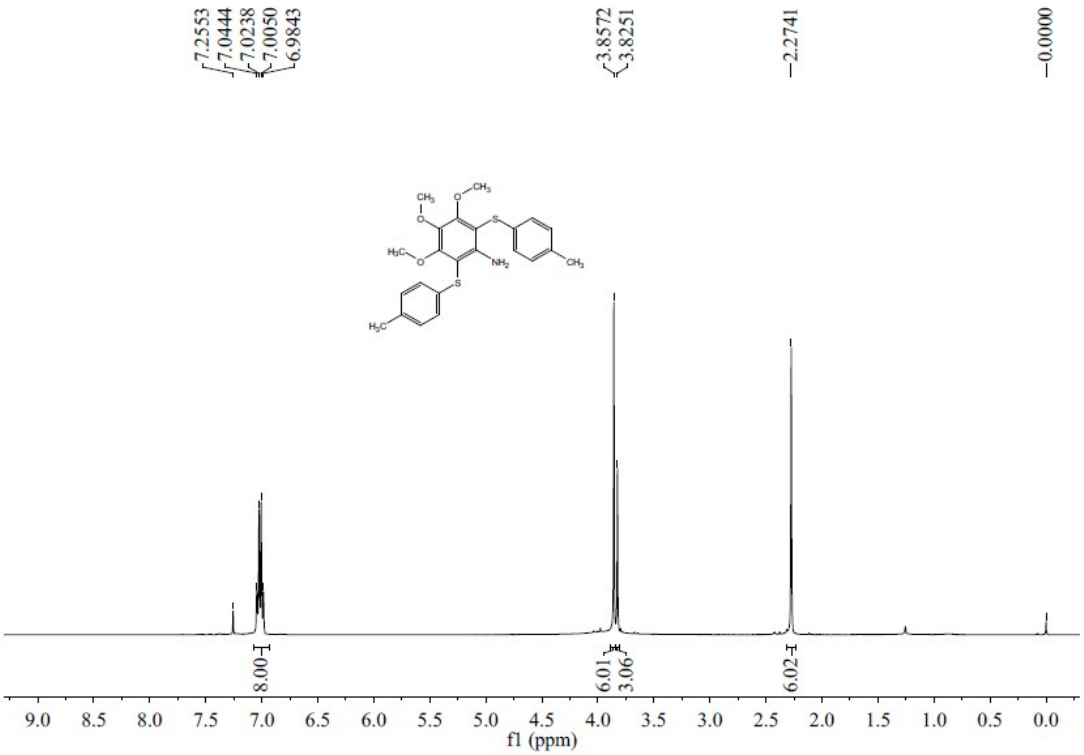
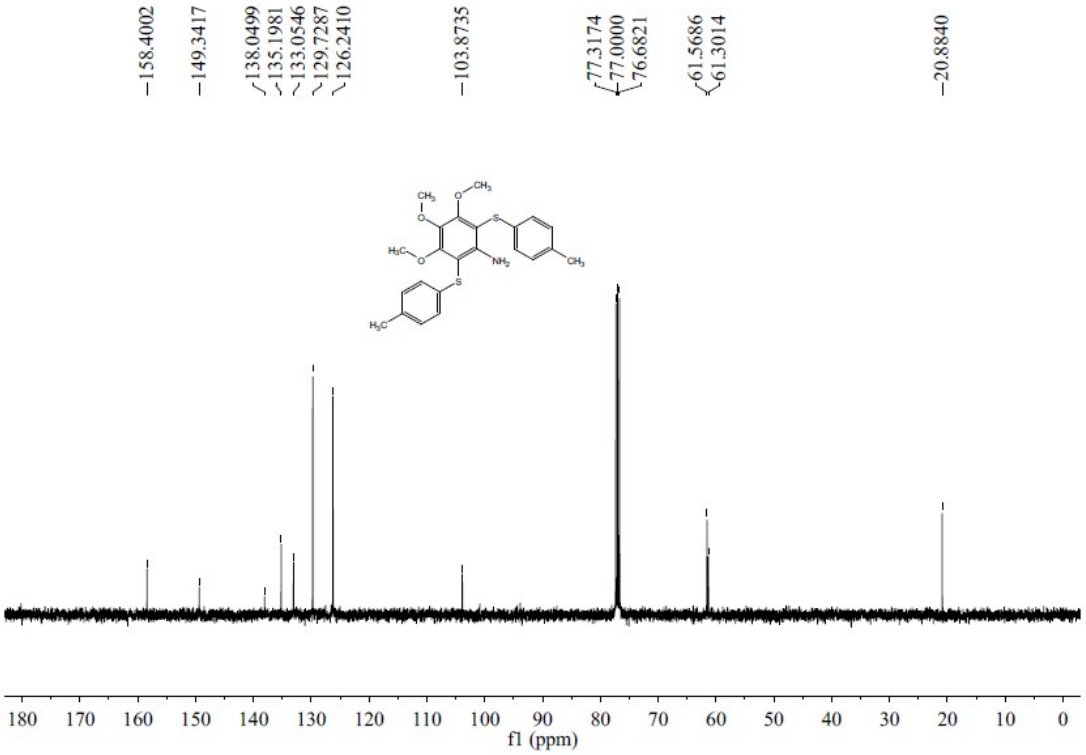


^{1}H NMR of **6ae**



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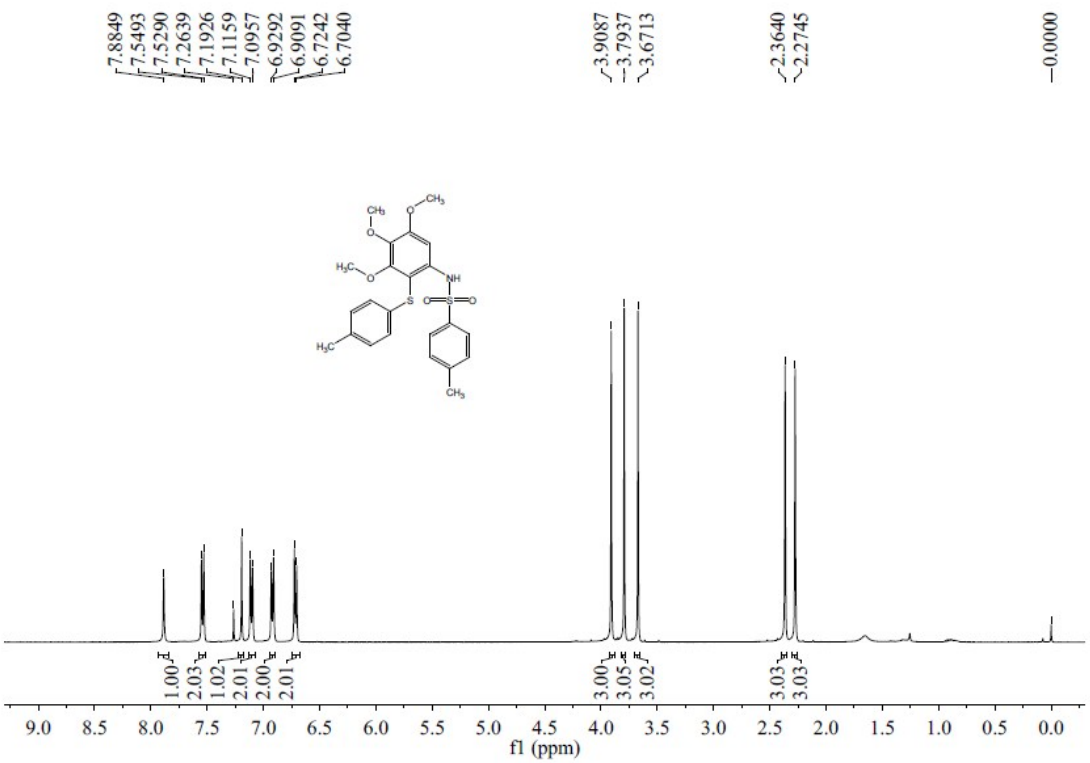

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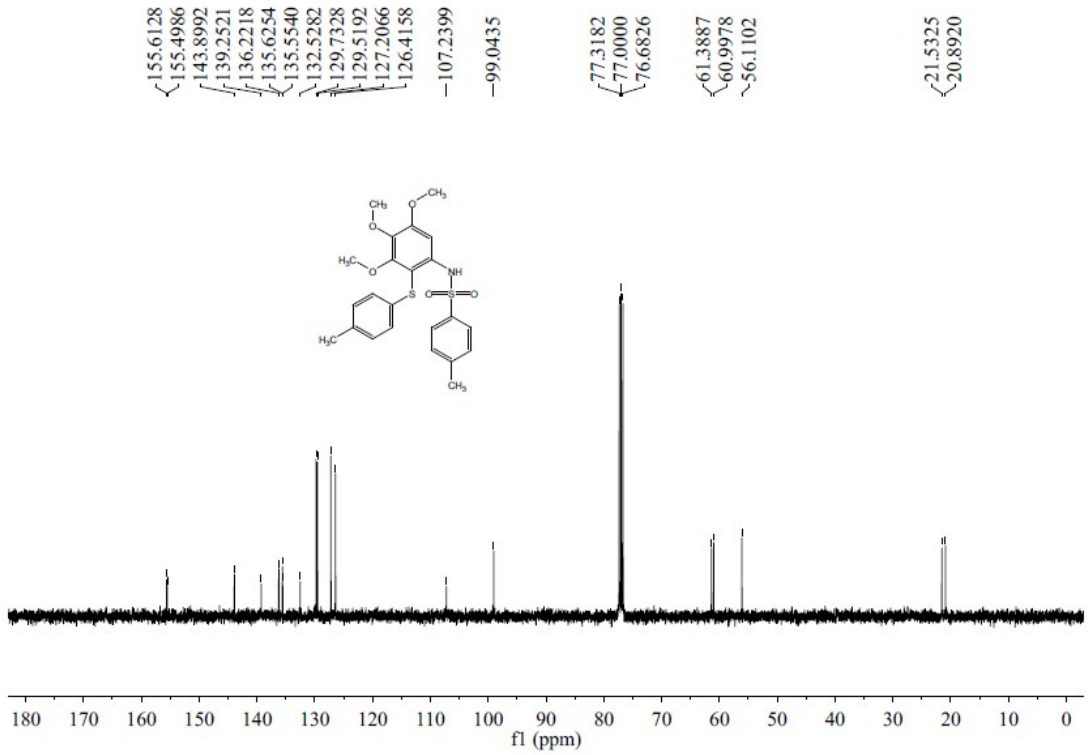

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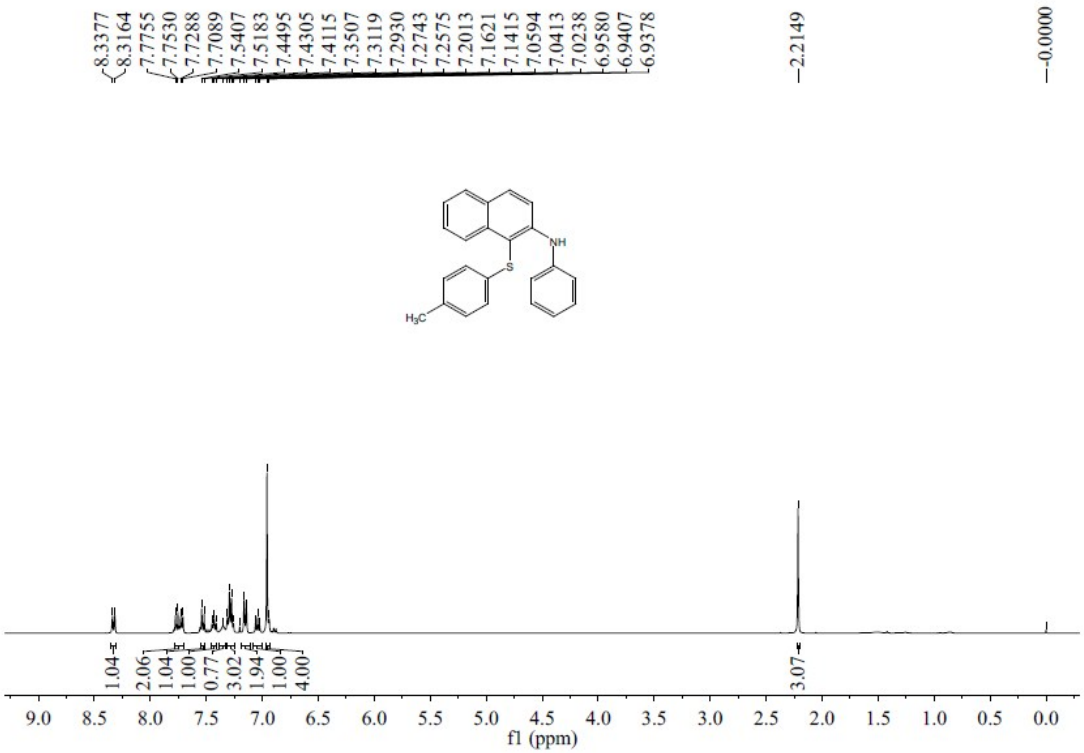
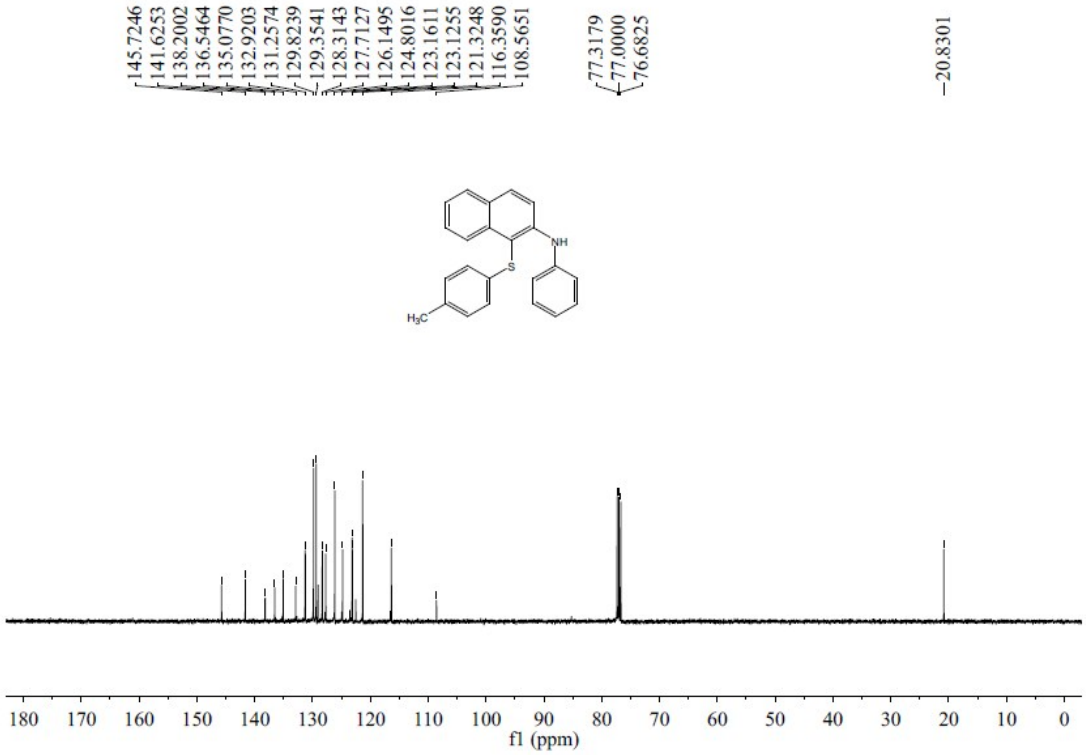
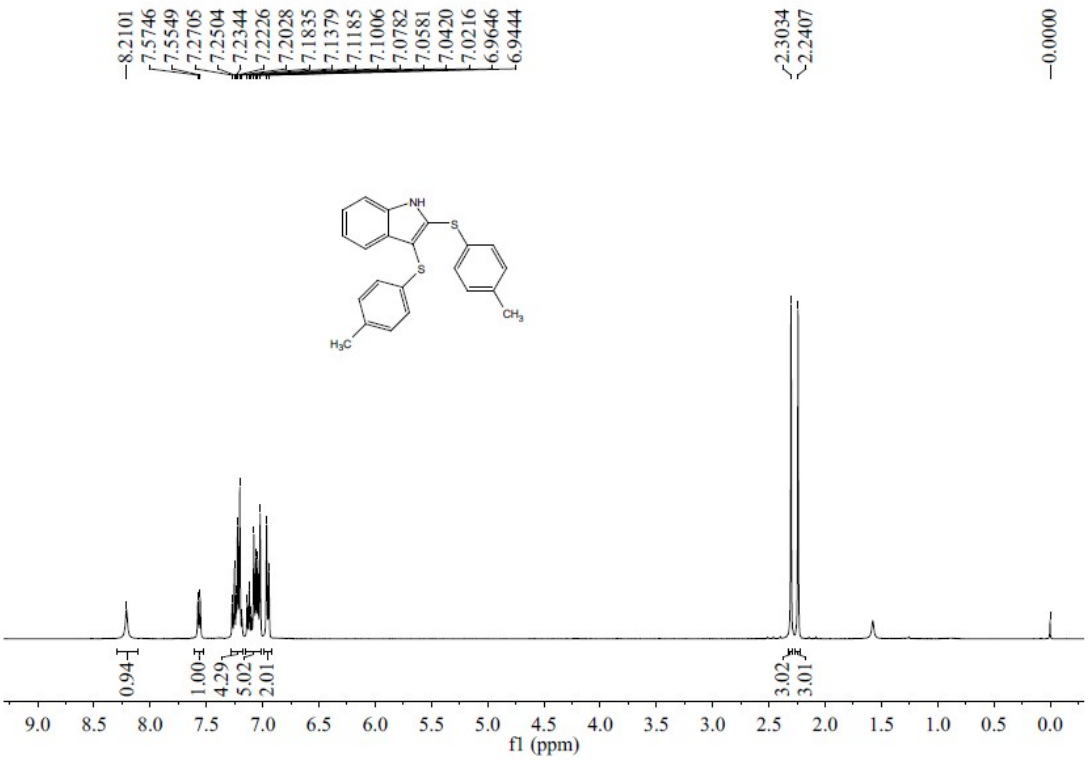


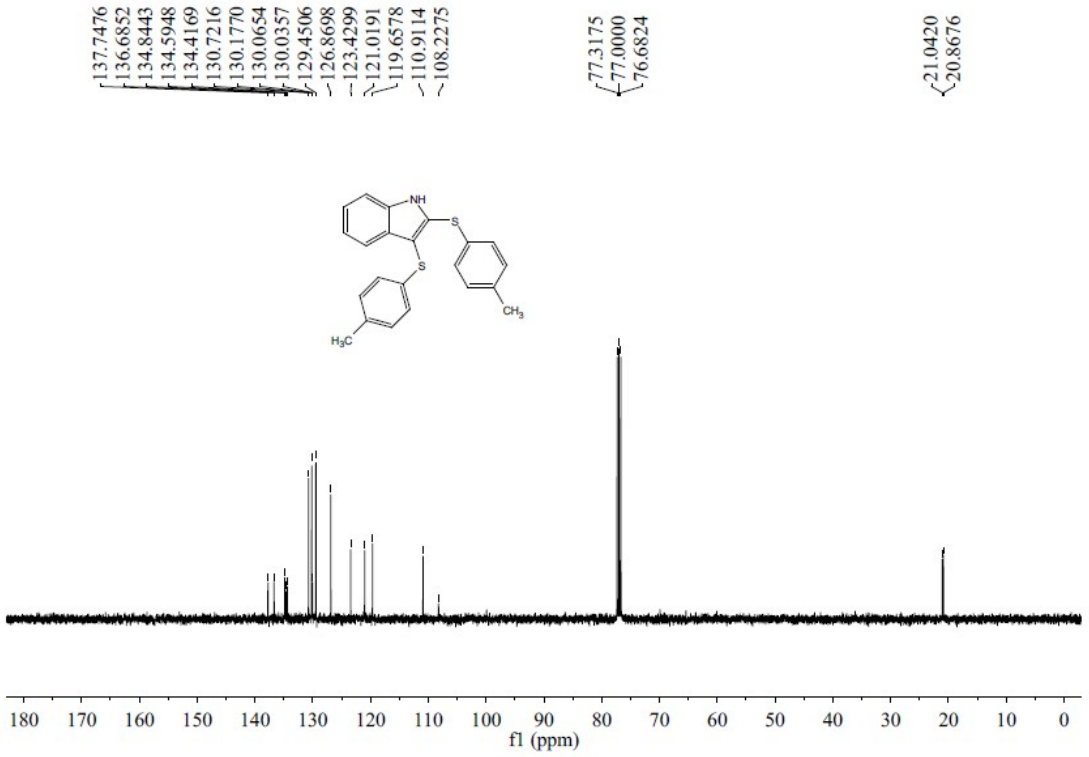
^{1}H NMR of **6ag**



^{13}C NMR of **6ag**



^{1}H NMR of **6ah**



^{13}C NMR of **6ah**